(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
30 June 2016 (30.06.2016)

WIPO | PCT

(10) **International Publication Number**
WO 2016/106086 A1

(51) **International Patent Classification**:
H01L 21/316 (2006.01) ***C07F 17/00*** (2006.01)
C07F 7/00 (2006.01) ***C07F 19/00*** (2006.01)
C07F 7/30 (2006.01) ***C23C 16/18*** (2006.01)

(21) **International Application Number**:
PCT/US2015/066434

(22) **International Filing Date**:
17 December 2015 (17.12.2015)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
14/580,324 23 December 2014 (23.12.2014) US

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,

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(54) **Title**: ZIRCONIUM-CONTAINING FILM FORMING COMPOSITIONS FOR VAPOR DEPOSITION OF ZIRCONIUM-CONTAINING FILMS

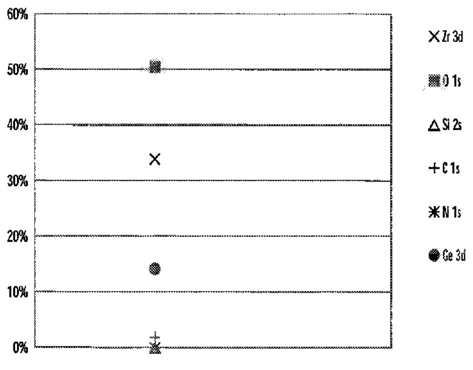
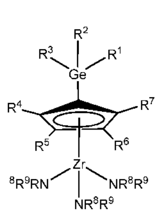
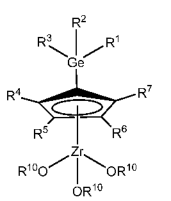


FIG. 12



(I)



(II)

(57) **Abstract**: Disclosed are Zirconium-containing film forming compositions comprising Germanium- and Zirconium-containing precursors having one of the following formulae: formula (I) and formula (II) wherein each R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} is independently selected from H; a C1-C5 linear, branched, or cyclic alkyl group; and a C1-C5 linear, branched, or cyclic fluoroalkyl groups. Also disclosed are methods of synthesizing the disclosed compositions and using the same to deposit Zirconium-containing films on substrates via vapor deposition processes.

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SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

ZIRCONIUM-CONTAINING FILM FORMING COMPOSITIONS FOR VAPOR DEPOSITION OF ZIRCONIUM-CONTAINING FILMS

Cross Reference to Related Applications

The present application claims the benefit of U.S. Application Serial No. 14/580,324 filed December 23, 2014, herein incorporated by reference in its entirety for all purposes.

Technical Field

Disclosed are Zirconium-containing film forming compositions comprising Germanium- and Zirconium-containing precursors. Also disclosed are methods of synthesizing the disclosed compositions and using the same to deposit Zirconium-containing films on substrates via vapor deposition processes.

Background

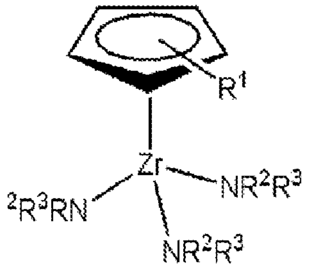
With the scaling down of semiconductor devices such as dynamic random access memory (DRAM), new materials with high dielectric constant are required. Indeed, in order to store a sufficient charge in a capacitor with a smaller surface area, capacitors with higher permittivity are needed. Among high-k dielectrics, Group 4 based materials, such as HfO_2 or ZrO_2, are very promising since their dielectric constant is higher than SiO_2 or Al_2O_3. However, their dielectric constant varies depending on their crystalline form (Thin Solid Films 486 (2005) 125-128).

Thick ZrO_2 layers tend to have an unstable crystalline phase and to have higher leakage current (Applied Physics Reviews (2012) version 14-9-2012). To prevent these defects, a thin layer of Al_2O_3 has been introduced in between two layers of ZrO_2, forming a so-called ZAZ capacitor, stabilizing the crystalline phase and reducing the leakage current (Applied Physics Letters 93, 033511 (2008); J. Vac. Sci. Techno. A 4 (6), 1986; Microelectronic Engineering 86 (2009) 1789-1795).

The cubic/tetragonal crystalline phase of the ZrO_2 layer, which is the phase having the highest k-value, has also been stabilized by doping ZrO_2 with a small amount of silicon or germanium (US2013/0208403A1 for silicon and Journal of

Applied Physics, 2009, 106, 024107; Microelectronic Engineering, 2009, 86, 1626; Applied Physics Letters, 2011, 99, 121909 for germanium).

Group 4 alkylamide precursors containing cyclopentadienyl ligands have been developed, such as the one show below (Dussarrat et al., WO2007/141059; Niinisto et al., Journal of Materials Chemistry (2008), 18(43), 5243-5247). These precursors show a higher thermal stability in comparison to tetrakis alkylamide precursors.



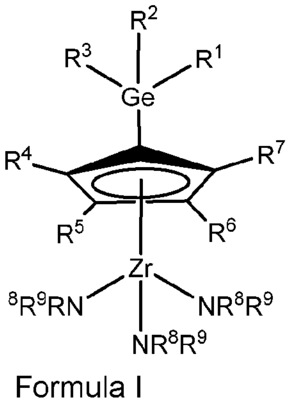
wherein R^1=H, Me, or Et; R^2&R^3=C_1-C_4 alkyl group

Similar to these compounds, a few germylcyclopentadienyl Group 4 compounds have been reported such as (trimethylgermyl)cyclopentadienyl tris(dimethylamino) Titanium(IV) (Journal of Organometallic Chemistry, 1975,101, 295).

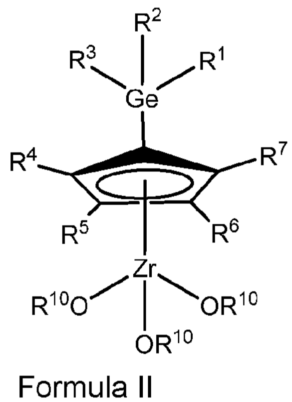
A need remains for developing liquid or low melting point (<50°C), highly thermally stable, with low viscosity, zirconium precursor molecules suitable for vapor phase thin film deposition with controlled thickness and composition at high temperature.

Summary

Disclosed are Zirconium-containing film forming compositions comprising a Germanium- and Zirconium-containing precursor having the following formula:



Formula I



Formula II

wherein each R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} is independently selected from H; a C1-C5 linear, branched, or cyclic alkyl group; or a C1-C5 linear, branched, or cyclic fluoroalkyl group. R^1, R^2 and R^3 may be identical or different. R^4, R^5, R^6 and R^7 may be identical or different. Each R^8 and R^9 may be identical or different. Each R^{10} may be identical or different. The disclosed Zirconium-containing film forming compositions may further include one or more of the following aspects:

- Each R^1 and R^2 and R^3 being independently selected from H, F, CF_3, Me, Et, nPr, iPr, nBu, iBu, sBu or tBu;
- Each R^4, R^5, R^6 and R^7 being independently selected from H, F, CF_3, Me, Et, nPr, iPr, nBu, iBu, sBu or tBu;
- Each R^8 and R^9 being independently selected from H, Me, Et, nPr, iPr, nBu, iBu, sBu or tBu;
- Each R^{10} being Me, Et, nPr, iPr, nBu, iBu, sBu, or tBu;
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr(TMG\text{-}Cp)(NMe_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr(TMG\text{-}Cp)(NHMe)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr(TMG\text{-}Cp)(NEt_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr(TMG\text{-}Cp)(NHEt)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(ethylmethylamino) Zirconium(IV) ($Zr(TMG\text{-}Cp)(NEtMe)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr(TMG\text{-}Cp)(NnPr_2)_3$);

- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr(TMG-Cp)(NiPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NnBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr(TMG-Cp)(NiBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHiBu)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NsBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NtBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHtBu)_3$);

- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) ($Zr(TMG\text{-}Cp)(OMe)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) ($Zr(TMG\text{-}Cp)(OEt)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) ($Zr(TMG\text{-}Cp)(OnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(iso-propoxy) Zirconium(IV) ($Zr(TMG\text{-}Cp)(OiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr(TMG\text{-}Cp)(OtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) ($Zr(TMG\text{-}Cp)(OsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) ($Zr(TMG\text{-}Cp)(OnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (trimethylgermyl)cyclopentadienyl tris(iso-butoxy) Zirconium(IV) ($Zr(TMG\text{-}Cp)(OiBu)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr(DMG\text{-}Cp)(NMe_2)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr(DMG\text{-}Cp)(NHMe)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr(DMG\text{-}Cp)(NEt_2)_3$);

- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHEt)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(ethylmethylamino) Zirconium(IV) ($Zr(DMG-Cp)(NEtMe)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr(DMG-Cp)(NnPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr(DMG-Cp)(NiPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr(DMG-Cp)(NnBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr(DMG-Cp)(NiBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHiBu)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr(DMG-Cp)(NsBu_2)_3$);

- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr(DMG\text{-}Cp)(NHsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr(DMG\text{-}Cp)(NtBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr(DMG\text{-}Cp)(NHtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) ($Zr(DMG\text{-}Cp)(OMe)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) ($Zr(DMG\text{-}Cp)(OEt)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) ($Zr(DMG\text{-}Cp)(OnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (dimethylgermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr(DMG\text{-}Cp)(OiPr)_3$);
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- the Germanium- and Zirconium-containing precursor being (trifluorogermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr(F_3Ge\text{-}Cp)(NMe_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trifluorogermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr(F_3Ge\text{-}Cp)(NHMe)_3$);
- the Germanium- and Zirconium-containing precursor being (trifluorogermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr(F_3Ge\text{-}Cp)(NEt_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trifluorogermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr(F_3Ge\text{-}Cp)(NHEt)_3$);
- the Germanium- and Zirconium-containing precursor being (trifluorogermyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) ($Zr(F_3Ge\text{-}Cp)(NEtMe)_3$);
- the Germanium- and Zirconium-containing precursor being (trifluorogermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr(F_3Ge\text{-}Cp)(NnPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trifluorogermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr(F_3Ge\text{-}Cp)(NHnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (trifluorogermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr(F_3Ge\text{-}Cp)(NiPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trifluorogermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr(F_3Ge\text{-}Cp)(NHiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (trifluorogermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr(F_3Ge\text{-}Cp)(NnBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (trifluorogermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr(F_3Ge\text{-}Cp)(NHnBu)_3$);

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- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NMe_2)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NHMe)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NEt_2)_3$);
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- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NHnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NiPr_2)_3$);

- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NHiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NnBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NHnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NiBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NHiBu)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NsBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NHsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NtBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(NHtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(OMe)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) ($Zr(F_2HGe\text{-}Cp)(OEt)_3$);

- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (difluorogermyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OiBu)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NMe_2)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHMe)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NEt_2)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHEt)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NEtMe)_3$);

- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NnPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NiPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NnBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NiBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHiBu)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NsBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NtBu_2)_3$);

- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr(FH_2Ge\text{-}Cp)(NHtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) ($Zr(FH_2Ge\text{-}Cp)(OMe)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) ($Zr(FH_2Ge\text{-}Cp)(OEt)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) ($Zr(FH_2Ge\text{-}Cp)(OnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr(FH_2Ge\text{-}Cp)(OiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr(FH_2Ge\text{-}Cp)(OtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) ($Zr(FH_2Ge\text{-}Cp)(OsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) ($Zr(FH_2Ge\text{-}Cp)(OnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (monofluorogermyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) ($Zr(FH_2Ge\text{-}Cp)(OiBu)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr(FMe_2Ge\text{-}Cp)(NMe_2)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr(FMe_2Ge\text{-}Cp)(NHMe)_3$);

- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NEt_2)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NHEt)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NEtMe)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NnPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NHnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NiPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NHiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NnBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NHnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NiBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NHiBu)_3$);

- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NsBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NHsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NtBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(NHtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(OMe)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(OEt)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(OnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(OiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(OtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(OsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(OnBu)_3$);

- the Germanium- and Zirconium-containing precursor being (fluoro dimethylgermyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) ($Zr(FMe_2Ge\text{-}Cp)(OiBu)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NMe_2)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NHMe)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NEt_2)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NHEt)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NEtMe)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NnPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NHnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NiPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NHiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NnBu_2)_3$);

- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NHnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NiBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NHiBu)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NsBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NHsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NtBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(NHtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(methoxy) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(OMe)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(OEt)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(OnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr((CF_3)_3Ge\text{-}Cp)(OiPr)_3$);

- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(OtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(OsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(OnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (tris(trifluoromethyl)germyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(OiBu)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NMe_2)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHMe)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NEt_2)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHEt)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NEtMe)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NnPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHnPr)_3$);

- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NiPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NnBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NiBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHiBu)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NsBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NtBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(methoxy) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(OMe)_3$);

- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) ($Zr((CF_3)_2HGe\text{-}Cp)(OEt)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) ($Zr((CF_3)_2HGe\text{-}Cp)(OnPr)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr((CF_3)_2HGe\text{-}Cp)(OiPr)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr((CF_3)_2HGe\text{-}Cp)(OtBu)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) ($Zr((CF_3)_2HGe\text{-}Cp)(OsBu)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) ($Zr((CF_3)_2HGe\text{-}Cp)(OnBu)_3$);
- the Germanium- and Zirconium-containing precursor being (bis(trifluoromethyl)germyl)cyclopentadienyl tris(iso-butoxy) Zirconium(IV) ($Zr((CF_3)_2HGe\text{-}Cp)(OiBu)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NMe_2)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHMe)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NEt_2)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHEt)_3$);

- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NEtMe)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NnPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHnPr)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NiPr_2)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHiPr)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NnBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHnBu)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NiBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHiBu)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NsBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHsBu)_3$);

- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NtBu_2)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHtBu)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OMe)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OEt)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OnPr)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OiPr)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OtBu)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OsBu)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OnBu)_3$);
- the Germanium- and Zirconium-containing precursor being ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OiBu)_3$);
- the Zirconium-containing film forming composition comprising between approximately 95% w/w and approximately 100% w/w of the precursor;

- the Zirconium-containing film forming composition comprising between approximately 98% w/w and approximately 100% w/w of the precursor;
- the Zirconium-containing film forming composition comprising between approximately 99% w/w and approximately 100% w/w of the precursor;
- the Zirconium-containing film forming composition comprising between approximately 5% w/w and approximately 50% w/w of the precursor;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 5.0% w/w impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 1.0% w/w impurities;
- the impurities including $ZrCp(OR^{10})_3$; $Zr(OR^{10})_4$; $ZrCp(NR_2)_3$, with each R independently being H, a C1-C5 linear, branched or cyclic alkyl group, or a C1-C5 linear, branched, or cyclic fluoroalkyl group; $Zr(NR_2)_4$, with each R independently being H, a C1-C5 linear, branched or cyclic alkyl group, or a C1-C5 linear, branched, or cyclic fluoroalkyl group; alcohol; alkylamines; dialkylamines; alkylimines; cyclopentadiene; dicyclopentadiene; (germyl)cyclopentadiene; alkylgermane; THF; ether; pentane; cyclohexane; heptanes; benzene; toluene; chlorinated metal compounds; lithium, sodium, or potassium alkylamino; lithium, sodium, or potassium alkoxy; and lithium, sodium, or potassium cyclopentadienyl;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w $ZrCp(OR^{10})_3$ impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w $Zr(OR^{10})_4$ impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w $ZrCp(NR_2)_3$ impurities, with each R independently being H, a C1-C5 linear, branched or cyclic alkyl group, or a C1-C5 linear, branched, or cyclic fluoroalkyl group;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w $Zr(NR_2)_4$ impurities,

with each R independently being H, a C1-C5 linear, branched or cyclic alkyl group, or a C1-C5 linear, branched, or cyclic fluoroalkyl group;

- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w alkylamine impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w alkylimine impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w alcohol impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w cyclopentadiene impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w dicyclopentadiene impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w (germyl)cyclopentadiene impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w alkylgermane impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w THF impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w ether impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w pentane impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w cyclohexane impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w heptanes impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w benzene impurities;

- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w toluene impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w chlorinated metal compound impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w lithium, sodium, or potassium cyclopentadienyl impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w lithium, sodium, or potassium alkylamino impurities;
- the Zirconium-containing film forming composition comprising between approximately 0.0% w/w and approximately 2.0% w/w lithium, sodium, or potassium alkoxy impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 1 ppmw metal impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw metal impurities;
- the metal impurities including Aluminum (Al), Arsenic (As), Barium (Ba), Beryllium (Be), Bismuth (Bi), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Cobalt (Co), Copper (Cu), Gallium (Ga), Germanium (Ge), Hafnium (Hf), Zirconium (Zr), Indium (In), Iron (Fe), Lead (Pb), Lithium (Li), Magnesium (Mg), Manganese (Mn), Tungsten (W), Nickel (Ni), Potassium (K), Sodium (Na), Strontium (Sr), Thorium (Th), Tin (Sn), Titanium (Ti), Uranium (U), and Zinc (Zn);
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Al impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw As impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Ba impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Be impurities;

- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Bi impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Cd impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Ca impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Cr impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Co impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Cu impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Ga impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Ge impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Hf impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Zr impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw In impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Fe impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Pb impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Li impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Mg impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Mn impurities;

- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw W impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Ni impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw K impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Na impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Sr impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Th impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Sn impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Ti impurities;
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw U impurities; and
- the Zirconium-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Zn impurities.

Also disclosed is a Zirconium-containing film forming composition delivery device comprising a canister having an inlet conduit and an outlet conduit and containing any of the Zirconium-containing film forming compositions disclosed above. The disclosed device may include one or more of the following aspects:

- the Zirconium-containing film forming composition having a total concentration of metal contaminants of less than 10 ppmw;
- an end of the inlet conduit end located above a surface of the Zirconium-containing film forming composition and an end of the outlet conduit located below the surface of the Zirconium-containing film forming composition;
- an end of the inlet conduit end located below a surface of the Zirconium-containing film forming composition and an end of the outlet conduit located above the surface of the Zirconium-containing film forming composition; and

- further comprising a diaphragm valve on the inlet and the outlet.

Also disclosed are processes for the deposition of Zirconium-containing films on substrates. The Zirconium-containing film forming compositions disclosed above are introduced into a reactor having a substrate disposed therein. At least part of the Germanium- and Zirconium-containing precursor is deposited onto the substrate to form the Zirconium-containing film. The disclosed processes may further include one or more of the following aspects:

- introducing a reactant into the reactor;
- the reactant being plasma-treated;
- the reactant being remote plasma-treated;
- the reactant not being plasma-treated;
- the reactant being selected from the group consisting of H_2, H_2CO, N_2H_4, NH_3, SiH_4, Si_2H_6, Si_3H_8, SiH_2Me_2, SiH_2Et_2, $N(SiH_3)_3$, hydrogen radicals thereof, and mixtures thereof;
- the reactant being H_2;
- the reactant being NH_3;
- the reactant being selected from the group consisting of O_2, O_3, H_2O, H_2O_2, NO, N_2O, NO_2, oxygen radicals thereof, and mixtures thereof;
- the reactant being O_3, $^1\Delta_g$ singlet oxygen, $^1\Sigma_g^+$ singlet oxygen, $^3\Sigma_g^-$ triplet oxygen, or combinations thereof;
- the reactant being H_2O;
- the reactant being plasma treated O_2;
- the reactant being O_3;
- the reactant being a Zirconium-containing precursor;
- the Zirconium-containing precursor being selected from the group consisting of $ZrCp(NMe_2)_3$, $Zr(MeCp)(NMe_2)_3$, $Zr(EtCp)(NMe_2)_3$, $Zr(iPrCp)(NMe_2)_3$, $Zr(tBuCp)(NMe_2)_3$, $Zr(Cp)(NMeEt)_3$;
- the Zirconium-containing precursor being $ZrCp(NMe_2)_3$;
- mixing the Zirconium-containing film forming composition and the Zirconium-containing precursor to form a mixture prior to introduction into the reactor;
- the Zirconium-containing film forming composition and the reactant being introduced into the reactor simultaneously;

- the reactor being configured for chemical vapor deposition;
- the reactor being configured for plasma enhanced chemical vapor deposition;
- the Zirconium-containing film forming composition and the reactant being introduced into the chamber sequentially;
- the reactor being configured for atomic layer deposition;
- the reactor being configured for plasma enhanced atomic layer deposition;
- the reactor being configured for spatial atomic layer deposition;
- the Zirconium-containing film being a pure Zirconium film;
- the pure Zirconium film having a Zr concentration between approximately 95 atomic% to approximately 100 atomic%;
- the Zirconium-containing film being a Zirconium silicide (Zr_kSi_l, wherein each of k and l is an integer which inclusively range from 1 to 6);
- the Zirconium silicide being $ZrSi_2$;
- the Zirconium-containing film being a Zirconium oxide (Zr_mO_n, wherein each of m and n is an integer which inclusively range from 1 to 6);
- the zirconium oxide being ZrO_2;
- the Zirconium-containing film being a Germanium-doped Zirconium oxide ($Zr_oGe_pO_q$), wherein each o and p is a decimal which inclusively ranges from 0 to 1 and q is an integer which inclusively ranges from 1 to 6);
- the germanium-doped Zirconium oxide being $Zr_{(0.99\text{ to }0.5)}Ge_{(0.5\text{ to }0.01)}O_2$;
- the Zirconium-containing film being a Zirconium nitride (Zr_uN_v, wherein each of u and v is an integer which inclusively range from 1 to 6); and
- the Zirconium nitride being ZrN.

Notation and Nomenclature

Certain abbreviations, symbols, and terms are used throughout the following description and claims, and include:

As used herein, the indefinite article "a" or "an" means one or more.

As used herein, the terms "approximately" or "about" or "*ca.*" (from the Latin "circa") mean ±10% of the value stated.

As used herein, the term "independently" when used in the context of describing R groups should be understood to denote that the subject R group is not only independently selected relative to other R groups bearing the same or different subscripts or superscripts, but is also independently selected relative to any additional species of that same R group. For example in the formula $Zr(TMGCp)(NR^1R^2)_3$, the three R^1 groups may, but need not be identical to each other or to R^2.

As used herein, the term “alkyl group” refers to saturated functional groups containing exclusively carbon and hydrogen atoms. Further, the term “alkyl group” refers to linear, branched, or cyclic alkyl groups. Examples of linear alkyl groups include without limitation, methyl groups, ethyl groups, propyl groups, butyl groups, etc. Examples of branched alkyls groups include without limitation, t-butyl. Examples of cyclic alkyl groups include without limitation, cyclopropyl groups, cyclopentyl groups, cyclohexyl groups, etc.

As used herein, the abbreviation “Me” refers to a methyl group; the abbreviation “Et” refers to an ethyl group; the abbreviation “Pr” refers to a propyl group; the abbreviation “nPr” refers to a “normal” or linear propyl group; the abbreviation “iPr” refers to an isopropyl group; the abbreviation “Bu” refers to a butyl group; the abbreviation “nBu” refers to a “normal” or linear butyl group; the abbreviation “tBu” refers to a tert-butyl group, also known as 1,1-dimethylethyl; the abbreviation “sBu” refers to a sec-butyl group, also known as 1-methylpropyl; the abbreviation “iBu” refers to an iso-butyl group, also known as 2-methylpropyl; the abbreviation “amyl” refers to an amyl or pentyl group; the abbreviation “tAmyl” refers to a tert-amyl group, also known as 1,1-dimethylpropyl; the abbreviation “Cp” refers to cyclopentadienyl; the abbreviation “Cp*” refers to pentamethylcyclopentadienyl; the abbreviation “op” refers to (open)pentadienyl; the abbreviation “TMGCp” refers to the ligand (trimethylgermyl)cyclopentadienyl [Me_3GeCp]; the abbreviation “TMGCpH” refers to the molecule (trimethylgermyl)cyclopentadiene [Me_3GeCpH]; the abbreviation DMGCp refers to the ligand (dimethylgermyl)cyclopentadienyl [Me_2HGeCp]; the abbreviation “TMSCp” refers to the ligand (trimethylsilyl)cyclopentadienyl [Me_3SiCp]; and the abbreviation “TMSCpH” refers to the molecule (trimethylsilyl)cyclopentadiene [Me_3SiCpH].

Please note that the films or layers deposited, such as Zirconium oxide, are listed throughout the specification and claims without reference to their proper stoichoimetry (i.e., ZrO_2). The layers may include pure (Zr) layers, carbide (Zr_oC_p) layers, nitride (Zr_kN_l) layers, oxide (Zr_nO_m) layers, or mixtures thereof, wherein k, l, m, n, o, and p inclusively range from 1 to 6. For instance, Zirconium oxide is Zr_kO_l, where k and l each range from 0.5 to 5. More preferably Zirconium oxide is ZrO_2. The oxide layer may be a mixture of different binary or ternary oxides layers. For example, the oxide layer may be $BaZrO_x$, $HfZrO_x$, $ZrYO_x$, $ZrAlO_x$, $ZrErO_x$, $ZrLaO_x$, $ZrDyO_x$, wherein x ranges from 1 to 6. The oxide layer may be a stack of different oxides layers, such as for example ZrO_2/Al_2O_3 nanolaminates. Any referenced layers may also include a Silicon oxide layer, Si_nO_m, wherein n ranges from 0.5 to 1.5 and m ranges from 1.5 to 3.5. More preferably, the silicon oxide layer is SiO_2 or SiO_3. The silicon oxide layer may be a silicon oxide based dielectric material, such as organic based or silicon oxide based low-k dielectric materials such as the Black Diamond II or III material by Applied Materials, Inc. Alternatively, any referenced silicon-containing layer may be pure silicon. Any silicon-containing layers may also include dopants, such as B, C, P, As and/or Ge.

The standard abbreviations of the elements from the periodic table of elements are used herein. It should be understood that elements may be referred to by these abbreviations (e.g., Ge refers to germanium, Si refers to silicon, C refers to carbon, etc.).

Brief Description of the Figures

For a further understanding of the nature and objects of the present invention, reference should be made to the following detailed description, taken in conjunction with the accompanying figure wherein:

FIG 1 is a side view of one embodiment of the Zirconium-containing film forming composition delivery device disclosed herein;

FIG 2 is a side view of a second embodiment of the Zirconium-containing film forming composition delivery device disclosed herein;

FIG 3 is a ^{1}HNMR spectrum of $Zr(TMGCp)(NMe_2)_3$;

FIG 4 is a ^{1}HNMR spectrum of $Zr(TMGCp)(OiPr)_3$;

FIG 5 is a ThermoGravimetric Analysis (TGA)/Differential Thermal Analysis (DTA) graph demonstrating the percentage of weight loss (TGA) or the differential temperature (DTA) with increasing temperature of $Zr(TMGCp)(NMe_2)_3$;

FIG 6 is a TGA/DTA graph demonstrating the percentage of weight loss (TGA) or the differential temperature (DTA) with increasing temperature of $Zr(TMGCp)(OiPr)_3$;

FIG 7 is a graph of the ALD growth rate of germanium silicon oxide thin film as a function of the temperature using the precursor $Zr(TMGCp)(NMe_2)_3$ and O_3 reactant;

FIG 8 is a graph of the X-ray Photoelectron Spectroscopy (XPS) analysis of the film produced as a function of temperature using the precursor $Zr(TMGCp)(NMe_2)_3$ and O_3 reactant;

Fig 9 is a Scanning Electron Microscope (SEM) photograph of the film deposited in a 1:10 aspect ratio pattern wafer using using the precursor $Zr(TMGCp)(NMe_2)_3$ at 325 °C;

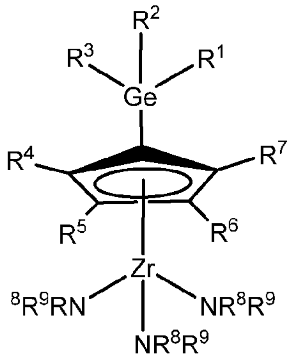
Fig 10 is a SEM photograph of the film deposited in a 1:40 aspect ratio pattern wafer using using the precursor $Zr(TMGCp)(NMe_2)_3$ at 325 °C;

FIG 11 is a graph of the ALD growth rate of germanium silicon oxide thin film as a function of the temperature using the precursor $Zr(TMGCp)(NMe_2)_3$ and H_2O reactant; and

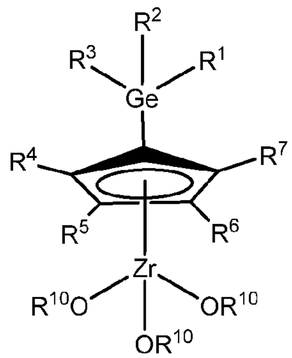
FIG 12 is a graph of the XPS analysis of the film produced at 300°C using the precursor $Zr(TMGCp)(NMe_2)_3$ and H_2O reactant.

Description of Preferred Embodiments

Disclosed are Zirconium-containing film forming compositions comprising a Germanium- and Zirconium-containing precursor having the following formula:



Formula I



Formula II

wherein each R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} is independently selected from H; a C1-C5 linear, branched, or cyclic alkyl group; or a C1-C5 linear, branched, or cyclic fluoroalkyl group. R^1, R^2 and R^3 may be identical or different. R^4, R^5, R^6 and R^7 may be identical or different. Each R^8 and R^9 may be identical or different. Each R^{10} may be identical or different.

Preferably R^1, R^2, R^3, R^4, R^5, R^6 and R^7 are H or Me because smaller alkyl groups may increase the volatility and decrease the melting point of the germanium- and zirconium-containing precursor. Preferably R^8 and R^9 are H, Me or Et because smaller alkyl groups may increase the volatility and decrease the melting point of the germanium- and zirconium-containing precursor. Preferably R^{10} is Me, Et, iPr or tBu because the smaller alkyl groups (Me, Et) may increase the volatility and the larger alkyl groups (iPr, tBu) may decrease the melting point of the germanium- and zirconium-containing precursor.

Exemplary Germanium- and Zirconium-containing precursors of Formula I include but are not limited to Zr(TMG-Cp)(NMe_2)$_3$, Zr(TMG-Cp)(NHMe)$_3$, Zr(TMG-Cp)(NEt_2)$_3$, Zr(TMG-Cp)(NHEt)$_3$, Zr(TMG-Cp)(NEtMe)$_3$), Zr(TMG-Cp)($NnPr_2$)$_3$, Zr(TMG-Cp)(NHnPr)$_3$, Zr(TMG-Cp)($NiPr_2$)$_3$, Zr(TMG-Cp)(NHiPr)$_3$, Zr(TMG-Cp)($NnBu_2$)$_3$), Zr(TMG-Cp)(NHnBu)$_3$, Zr(TMG-Cp)($NiBu_2$)$_3$, Zr(TMG-Cp)(NHiBu)$_3$, Zr(TMG-Cp)($NsBu_2$)$_3$, Zr(TMSG-Cp)(NHsBu)$_3$, Zr(TMG-Cp)($NtBu_2$)$_3$, Zr(TMG-Cp)(NHtBu)$_3$, Zr(DMG-Cp)(NMe_2)$_3$, Zr(DMG-Cp)(NHMe)$_3$, Zr(DMG-Cp)(NEt_2)$_3$, Zr(DMG-Cp)(NHEt)$_3$, Zr(DMG-Cp)(NEtMe)$_3$, Zr(DMG-Cp)($NnPr_2$)$_3$, Zr(DMG-Cp)(NHnPr)$_3$, Zr(DMG-Cp)($NiPr_2$)$_3$, Zr(DMG-Cp)(NHiPr)$_3$, Zr(DMG-Cp)($NnBu_2$)$_3$, Zr(DMG-Cp)(NHnBu)$_3$, Zr(DMG-Cp)($NiBu_2$)$_3$, Zr(DMG-Cp)(NHiBu)$_3$, Zr(DMG-Cp)($NsBu_2$)$_3$, Zr(DMG-Cp)(NHsBu)$_3$, Zr(DMG-Cp)($NtBu_2$)$_3$, Zr(DMG-Cp)(NHtBu)$_3$, Zr(F_3Ge-Cp)(NMe_2)$_3$, Zr(F_3Ge-Cp)(NHMe)$_3$, Zr(F_3Ge-Cp)(NEt_2)$_3$, Zr(F_3Ge-Cp)(NHEt)$_3$, Zr(F_3Ge-Cp)(NEtMe)$_3$, Zr(F_3Ge-Cp)($NnPr_2$)$_3$, Zr(F_3Ge-Cp)(NHnPr)$_3$, Zr(F_3Ge-Cp)($NiPr_2$)$_3$, Zr(F_3Ge-Cp)(NHiPr)$_3$, Zr(F_3Ge-Cp)($NnBu_2$)$_3$, Zr(F_3Ge-Cp)(NHnBu)$_3$, Zr(F_3Ge-Cp)($NiBu_2$)$_3$, Zr(F_3Ge-Cp)(NHiBu)$_3$, Zr(F_3Ge-Cp)($NsBu_2$)$_3$, Zr(F_3Ge-Cp)(NHsBu)$_3$, Zr(F_3Ge-Cp)($NtBu_2$)$_3$, Zr(F_3Ge-Cp)(NHtBu)$_3$, Zr(F_2HGe-Cp)(NMe_2)$_3$, Zr(F_2HGe-Cp)(NHMe)$_3$, Zr(F_2HGe-Cp)(NEt_2)$_3$, Zr(F_2HGe-Cp)(NHEt)$_3$, Zr(F_2HGe-Cp)(NEtMe)$_3$, Zr(F_2HGe-Cp)($NnPr_2$)$_3$, Zr(F_2HGe-Cp)(NHnPr)$_3$, Zr(F_2HGe-Cp)($NiPr_2$)$_3$, Zr(F_2HGe-Cp)(NHiPr)$_3$, Zr(F_2HGe-Cp)($NnBu_2$)$_3$, Zr(F_2HGe-Cp)(NHnBu)$_3$, Zr(F_2HGe-Cp)($NiBu_2$)$_3$, Zr(F_2HGe-Cp)(NHiBu)$_3$, Zr(F_2HGe-Cp)($NsBu_2$)$_3$, Zr(F_2HGe-Cp)(NHsBu)$_3$, Zr(F_2HGe-Cp)($NtBu_2$)$_3$, Zr(F_2HGe-Cp)(NHtBu)$_3$, Zr(FH_2Ge-Cp)(NMe_2)$_3$, Zr(FH_2Ge-Cp)(NHMe)$_3$, Zr(FH_2Ge-

$Cp)(NEt_2)_3$, $Zr(FH_2Ge\text{-}Cp)(NHEt)_3$, $Zr(FH_2Ge\text{-}Cp)(NEtMe)_3$, $Zr(FH_2Ge\text{-}Cp)(NnPr_2)_3$, $Zr(FH_2Ge\text{-}Cp)(NHnPr)_3$, $Zr(FH_2Ge\text{-}Cp)(NiPr_2)_3$, $Zr(FH_2Ge\text{-}Cp)(NHiPr)_3$, $Zr(FH_2Ge\text{-}Cp)(NnBu_2)_3$, $Zr(FH_2Ge\text{-}Cp)(NHnBu)_3$, $Zr(FH_2Ge\text{-}Cp)(NiBu_2)_3$, $Zr(FH_2Ge\text{-}Cp)(NHiBu)_3$, $Zr(FH_2Ge\text{-}Cp)(NsBu_2)_3$, $Zr(FH_2Ge\text{-}Cp)(NHsBu)_3$, $Zr(FH_2Ge\text{-}Cp)(NtBu_2)_3$, $Zr(FH_2Ge\text{-}Cp)(NHtBu)_3$, $Zr(FMe_2Ge\text{-}Cp)(NMe_2)_3$, $Zr(FMe_2Ge\text{-}Cp)(NHMe)_3$, $Zr(FMe_2Ge\text{-}Cp)(NEt_2)_3$, $Zr(FMe_2Ge\text{-}Cp)(NHEt)_3$, $Zr(FMe_2Ge\text{-}Cp)(NEtMe)_3$, $Zr(FMe_2Ge\text{-}Cp)(NnPr_2)_3$, $Zr(FMe_2Ge\text{-}Cp)(NHnPr)_3$, $Zr(FMe_2Ge\text{-}Cp)(NiPr_2)_3$, $Zr(FMe_2Ge\text{-}Cp)(NHiPr)_3$, $Zr(FMe_2Ge\text{-}Cp)(NnBu_2)_3$, $Zr(FMe_2Ge\text{-}Cp)(NHnBu)_3$, $Zr(FMe_2Ge\text{-}Cp)(NiBu_2)_3$, $Zr(FMe_2Ge\text{-}Cp)(NHiBu)_3$, $Zr(FMe_2Ge\text{-}Cp)(NsBu_2)_3$, $Zr(FMe_2Ge\text{-}Cp)(NHsBu)_3$, $Zr(FMe_2Ge\text{-}Cp)(NtBu_2)_3$, $Zr(FMe_2Ge\text{-}Cp)(NHtBu)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NMe_2)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NHMe)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NEt_2)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NHEt)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NEtMe)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NnPr_2)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NHnPr)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NiPr_2)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NHiPr)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NnBu_2)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NHnBu)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NiBu_2)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NHiBu)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NsBu_2)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NHsBu)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NtBu_2)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(NHtBu)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NMe)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NHMe)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NEt_2)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NHEt)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NEtMe)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NnPr_2)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NHnPr)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NiPr_2)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NHiPr)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NnBu_2)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NHnBu)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NiBu_2)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NHiBu)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NsBu_2)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NHsBu)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NtBu_2)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(NHtBu)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NMe_2)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NHMe)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NEt_2)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NHEt)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NEtMe)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NnPr_2)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NHnPr)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NiPr_2)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NHiPr)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NnBu_2)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NHnBu)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NiBu_2)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NHiBu)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NsBu_2)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NHsBu)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(NtBu_2)_3$, or $Zr((CF_3)Me_2Ge\text{-}Cp)(NHtBu)_3$.

Exemplary Germanium- and Zirconium-containing precursors of Formula II include but are not limited to $Zr(TMG\text{-}Cp)(OMe)_3$, $Zr(TMG\text{-}Cp)(OEt)_3$, $Zr(TMG\text{-}Cp)(OnPr)_3$, $Zr(TMG\text{-}Cp)(OiPr)_3$, $Zr(TMG\text{-}Cp)(OtBu)_3$, $Zr(TMG\text{-}Cp)(OsBu)_3$,

$Zr(TMG\text{-}Cp)(OnBu)_3$, $Zr(TMG\text{-}Cp)(OiBu)_3$, $Zr(DMG\text{-}Cp)(OMe)_3$, $Zr(DMG\text{-}Cp)(OEt)_3$, $Zr(DMG\text{-}Cp)(OnPr)_3$, $Zr(DMG\text{-}Cp)(OiPr)_3$, $Zr(DMG\text{-}Cp)(OtBu)_3$, $Zr(DMG\text{-}Cp)(OsBu)_3$, $Zr(DMG\text{-}Cp)(OnBu)_3$, $Zr(DMG\text{-}Cp)(OiBu)_3$, $Zr(F_3Ge\text{-}Cp)(OMe)_3$, $Zr(F_3Ge\text{-}Cp)(OEt)_3$, $Zr(F_3Ge\text{-}Cp)(OnPr)_3$, $Zr(F_3Ge\text{-}Cp)(OiPr)_3$, $Zr(F_3Ge\text{-}Cp)(OtBu)_3$, $Zr(F_3Ge\text{-}Cp)(OsBu)_3$,$Zr(F_3Ge\text{-}Cp)(OnBu)_3$, $Zr(F_3Ge\text{-}Cp)(OiBu)_3$, $Zr(F_2HGe\text{-}Cp)(OMe)_3$, $Zr(F_2HGe\text{-}Cp)(OEt)_3$, $Zr(F_2HGe\text{-}Cp)(OnPr)_3$, $Zr(F_2HGe\text{-}Cp)(OiPr)_3$, $Zr(F_2HGe\text{-}Cp)(OtBu)_3$, $Zr(F_2HGe\text{-}Cp)(OsBu)_3$, $Zr(F_2HGe\text{-}Cp)(OnBu)_3$, $Zr(F_2HGe\text{-}Cp)(OiBu)_3$, $Zr(FH_2Ge\text{-}Cp)(OMe)_3$, $Zr(FH_2Ge\text{-}Cp)(OEt)_3$, $Zr(FH_2Ge\text{-}Cp)(OnPr)_3$, $Zr(FH_2Ge\text{-}Cp)(OiPr)_3$, $Zr(FH_2Ge\text{-}Cp)(OtBu)_3$, $Zr(FH_2Ge\text{-}Cp)(OsBu)_3$, $Zr(FH_2Ge\text{-}Cp)(OnBu)_3$, $Zr(FH_2Ge\text{-}Cp)(OiBu)_3$, $Zr(FMe_2Ge\text{-}Cp)(OMe)_3$, $Zr(FMe_2Ge\text{-}Cp)(OEt)_3$, $Zr(FMe_2Ge\text{-}Cp)(OnPr)_3$, $Zr(FMe_2Ge\text{-}Cp)(OiPr)_3$, $Zr(FMe_2Ge\text{-}Cp)(OtBu)_3$, $Zr(FMe_2Ge\text{-}Cp)(OsBu)_3$, $Zr(FMe_2Ge\text{-}Cp)(OnBu)_3$, $Zr(FMe_2Ge\text{-}Cp)(OiBu)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(OMe)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(OEt)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(OnPr)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(OiPr)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(OtBu)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(OsBu)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(OnBu)_3$, $Zr((CF_3)_3Ge\text{-}Cp)(OiBu)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(OMe)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(OEt)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(OnPr)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(OiPr)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(OtBu)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(OsBu)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(OnBu)_3$, $Zr((CF_3)_2HGe\text{-}Cp)(OiBu)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(OMe)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(OEt)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(OnPr)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(OiPr)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(OtBu)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(OsBu)_3$, $Zr((CF_3)Me_2Ge\text{-}Cp)(OnBu)_3$, or $Zr((CF_3)Me_2Ge\text{-}Cp)(OiBu)_3$.

Preferably, the Germanium- and Zirconium-containing precursor is (trimethylgermyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV), due to its vaporization results in atmospheric thermo gravimetric analysis, leaving a small amount of final residue (see Example 1). The low amount of residue demonstrated by the TGA results for (trimethylgermyl)cyclopentadienyl tri(isopropoxy) Zirconium (IV) in Example 2 are also promising for vapor deposition applications.

The disclosed Zirconium-containing film forming compositions may be synthesized by reacting the corresponding tetrakis(amino) Zirconium(IV) or corresponding tetrakis(alkoxy) Zirconium(IV) with the corresponding (germyl)cyclopentadiene in a suitable solvent, such as toluene, THF or ether. (Germyl)cyclopentadiene are typically prepared according to the procedure described in Organometallics 1990, 9, 2488-2492. Alternatively the disclosed (germyl)cyclopentadienyl-tris(alkoxy) Zirconium-containing compounds may be synthesized by alcoholysis of the corresponding (germyl)cyclopentadienyl-tris(amino) Zirconium-containing compounds with 3 equivalents of the corresponding alcohol in a suitable solvent, such as toluene, THF or ether. However, an excess of alcohol in this synthesis process may result in unreacted reactants, such as $Zr(NR_2)_4$ or $Zr(OR)_4$, and unwanted reaction by-products, such as unsubstituted cyclopentadienyl reaction products like cyclopentadienyl tris(alkoxy) zirconium or cyclopentadienyl tris(amino) zirconium. Exemplary synthesis methods containing further details are provided in the Examples that follow.

Purity of the disclosed Zirconium-containing film forming compositions ranges from approximately 95% w/w to approximately 100% w/w, preferably higher than 98% w/w, and more preferably higher than 99% w/w. One of ordinary skill in the art will recognize that the purity may be determined by H NMR or gas or liquid chromatography with mass spectrometry. The disclosed Zirconium-containing film forming compositions may contain any of the following impurities: $ZrCp(OR^{10})_3$; $Zr(OR^{10})_4$; $ZrCp(NR_2)_3$, with each R independently being H, a C1-C5 linear, branched or cyclic alkyl group, or a C1-C5 linear, branched, or cyclic fluoroalkyl group; $Zr(NR_2)_4$, with each R independently being H, a C1-C5 linear, branched or cyclic alkyl group, or a C1-C5 linear, branched, or cyclic fluoroalkyl group; alcohol, such as isopropyl alcohol or tert-butyl alcohol; cyclopentadiene; (germyl)cyclopentadiene; dicyclopentadiene; alkylgermane; alkylamines such as tert-butylamine; dialkylamines such as dimethylamine; alkylimines; THF; ether; pentane; cyclohexane; heptanes; benzene; toluene; chlorinated metal compounds; lithium, sodium or potassium alkoxy; lithium, sodium, or potassium alkylamino; or lithium, sodium, or potassium cyclopentadienyl. The total quantity of these impurities ranges from approximately 0% w/w to approximately 5% w/w, preferably below 2% w/w, and more preferably below 1% w/w. The composition may be purified by recrystallisation, sublimation, distillation, and/or passing the gas or liquid through a suitable adsorbent, such as a 4A molecular sieve.

Purification of the disclosed Zirconium-containing film forming compositions may also result in metal impurities at the 0 ppbw (parts per billion weight) to 1 ppmw (parts per million weight) levels, preferably 0-500 ppbw level. These metal impurities include, but are not limited to, Aluminum (Al), Arsenic (As), Barium (Ba), Beryllium (Be), Bismuth (Bi), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Cobalt (Co), Copper (Cu), Gallium (Ga), Germanium (Ge), Hafnium (Hf), Zirconium (Zr), Indium (In), Iron (Fe), Lead (Pb), Lithium (Li), Magnesium (Mg), Manganese (Mn), Tungsten (W), Nickel (Ni), Potassium (K), Sodium (Na), Strontium (Sr), Thorium (Th), Tin (Sn), Titanium (Ti), Uranium (U), Vanadium (V) and Zinc (Zn).

The Zirconium-containing film forming compositions may be delivered to a semiconductor processing tool by the disclosed Zirconium-containing film forming composition delivery devices. **FIGS 1 and 2** show two non-limiting embodiments of the disclosed delivery devices **1**.

FIG 1 is a side view of one embodiment of the Zirconium-containing film forming composition delivery device **1**. In **FIG 1**, the disclosed Zirconium-containing film forming compositions **10** are contained within a container **20** having two conduits, an inlet conduit **30** and an outlet conduit **40**. One of ordinary skill in the precursor art will recognize that the container **20**, inlet conduit **30**, and outlet conduit **40** are manufactured to prevent the escape of the gaseous form of the Zirconium-containing film forming composition **10**, even at elevated temperature and pressure.

The delivery device **1** must be leak tight and be equipped with valves **35/45** that do not permit escape of even minute amounts of the material. Suitable valves **35/45** include spring-loaded or tied diaphragm valves. The valves **35/45** may further comprise a restrictive flow orifice (RFO). The delivery device **1** may be connected to a gas manifold (not shown) and in an enclosure (not shown). The gas manifold should permit the safe evacuation and purging of the piping that may be exposed to Air when the delivery device **1** is replaced so that any residual amounts of the Zr-containing film forming composition does not react. The enclosure may be equipped with sensors and fire control capability to control the fire in the case of material release or reaction. The gas manifold may also be equipped with isolation valves, vacuum generators, and permit the introduction of a purge gas at a minimum.

The delivery device **1** fluidly connects to other components of the semiconductor processing tool, such as the gas cabinet disclosed above, via valves **35** and **45**. Preferably, the container **20**, inlet conduit **30**, valve **35**, outlet conduit **40**, and valve **45** are made of 316L EP or 304 stainless steel. However, one of ordinary skill in the art will recognize that other non-reactive materials may also be used in the teachings herein and that any corrosive Zirconium-containing film forming compositions **10** may require the use of more corrosion-resistant materials, such as Hastelloy or Inconel.

In **FIG 1**, the end **31** of inlet conduit **30** is located above the surface of the Zirconium-containing film forming composition **10**, whereas the end **41** of the outlet conduit **40** is located below the surface of the Zirconium-containing film forming composition **10**. In this embodiment, the Zirconium-containing film forming composition **10** is preferably in liquid form. An inert gas, including but not limited to nitrogen, argon, helium, and mixtures thereof, may be introduced into the inlet conduit **30**. The inert gas pressurizes the delivery device **20** so that the liquid Zirconium-containing film forming composition **10** is forced through the outlet conduit **40** and to components in the semiconductor processing tool (not shown). The semiconductor processing tool may include a vaporizer which transforms the liquid Zirconium-containing film forming composition **10** into a vapor, with or without the use of a carrier gas such as helium, argon, nitrogen or mixtures thereof, in order to deliver the vapor to a chamber where a wafer to be repaired is located and treatment occurs in the vapor phase. Alternatively, the liquid Zirconium-containing film forming composition **10** may be delivered directly to the wafer surface as a jet or aerosol.

FIG 2 is a side view of a second embodiment of the Zirconium-containing film forming composition delivery device **1**. In **FIG 2**, the end **31** of inlet conduit **30** is located below the surface of the Zirconium-containing film forming composition **10**, whereas the end **41** of the outlet conduit **40** is located above the surface of the Zirconium-containing film forming composition **10**. **FIG 2** also includes an optional heating element **25**, which may increase the temperature of the Zirconium-containing film forming composition **10**. In this embodiment, the Zirconium-containing film forming composition **10** may be in solid or liquid form. An inert gas, including but not limited to nitrogen, argon, helium, and mixtures thereof, is introduced into the inlet conduit **30**. The inert gas bubbles through the Zirconium-containing film forming composition **10** and carries a mixture of the inert gas and vaporized Zirconium-containing film forming composition **10** to the outlet conduit **40** and on to the components in the semiconductor processing tool.

Both **FIGS 1 and 2** include valves **35** and **45**. One of ordinary skill in the art will recognize that valves **35** and **45** may be placed in an open or closed position to allow flow through conduits **30** and **40**, respectively. Either delivery device **1** in **FIGS 1 or 2**, or a simpler delivery device having a single conduit terminating above the surface of any solid or liquid present, may be used if the Zirconium-containing film forming composition **10** is in vapor form or if sufficient vapor pressure is present above the solid/liquid phase. In this case, the Zirconium-containing film forming composition **10** is delivered in vapor form through the conduit **40** simply by opening the valve **45**. The delivery device **1** may be maintained at a suitable temperature to provide sufficient vapor pressure for the Zirconium-containing film forming composition **10** to be delivered in vapor form, for example by the use of an optional heating element **25**.

While **FIGS 1 and 2** disclose two embodiments of the Zirconium-containing film forming composition delivery device **1**, one of ordinary skill in the art will recognize that the inlet conduit **30** and outlet conduit **40** may both be located above or below the surface **11** of the Zirconium-containing film forming composition **10** without departing from the disclosure herein. Furthermore, inlet conduit **30** may be a filling port. Finally, one of ordinary skill in the art will recognize that the disclosed Zirconium-containing film forming composition may be delivered to semiconductor processing tools using other delivery devices, such as the ampoules disclosed in WO 2006/059187 to Jurcik et al., without departing from the teachings herein.

Also disclosed are methods for forming Zirconium-containing layers on a substrate using a vapor deposition process. The method may be useful in the manufacture of semiconductor, photovoltaic, LCD-TFT, or flat panel type devices. The disclosed Zirconium-containing film forming compositions may be used to deposit thin Zirconium-containing films using any deposition methods known to those of skill in the art.

Examples of suitable deposition methods include, without limitation, chemical vapor deposition (CVD) or atomic layer deposition (ALD). Exemplary CVD methods include thermal CVD, plasma enhanced CVD (PECVD), pulsed

CVD (PCVD), low pressure CVD (LPCVD), sub-atmospheric CVD (SACVD), atmospheric pressure CVD (APCVD), hot-wire CVD (HWCVD, also known as cat-CVD, in which a hot wire serves as an energy source for the deposition process), radicals incorporated CVD, and combinations thereof. Exemplary ALD methods include thermal ALD, plasma enhanced ALD (PEALD), spatial isolation ALD, hot-wire ALD (HWALD), radicals incorporated ALD, and combinations thereof. Supercritical fluid deposition may also be used. The deposition method is preferably ALD, PE-ALD, or spatial ALD in order to provide suitable step coverage and film thickness control.

The cubic/tetragonal crystalline phase of ZrO_2 provides the highest dielectric constant of the different ZrO_2 crystalline forms (cubic, tetragonal, amorphous, monoclinic, orthorhombic, and combinations thereof are the available crystalline phases). It is experimentally reported that a doping level (3-12%) of small ionic radius tetravalent dopant such as Ge is the most efficient in stabilizing the tetragonal zirconia phase. The substitution of a Zr atom by Ge in the tetragonal ZrO_2 structure results in reduced Ge–O bond with length similar to that in GeO_2. Therefore, ZrO_2 is an excellent host for Ge, which is easily incorporated into the “friendly” local environment of the oxide (J. Appl. Phys. 106, 024107, 2009). The advantage is that Ge is tetravalent therefore it substitutes Zr in the lattice without introducing O vacancies. The preliminary R&D test results provided in Example 4 show that deposition using $Zr(Me_3GeCp)(NMe_2)_3$ produced 14 atomic % Ge with little impurity contamination, demonstrating the potential of the these precursors to be able to deposit the desired crystalline phase of the zirconium oxide films.

Applicants believe that the vapor deposition process conditions may be controlled so that Zr alone or both Zr and Ge may be deposited in the zirconium-containing layer. For instance, adjusting the ALD parameters to exhibit some parasitic CVD might be useful to deposit a finite amount of Ge in the ZrO_2 layer. Alternatively, the germanium content in ZrO_2 film may be controlled by alternating the deposition of $(Zr, Ge)O_2$ film using the disclosed Zirconium-containing film forming compositions and the deposition of ZrO_2 using another zirconium-containing precursor. For example, $ZrCp(NMe_2)_3$, $Zr(MeCp)(NMe_2)_3$ or $Zr(EtCp)(NMe_2)_3$ may serve as the Zr-containing precursor to produce ZrO_2 films.

In other words *x* subcycles of (Zr, Ge)O_2 deposition using the Zirconium-containing film forming compositions may be alternated with *y* subcycles of ZrO_2 deposition using a zirconium-containing precursor, such as $ZrCp(NMe_2)_3$. The supercycle consisting of *x* subcycles of (Zr, Ge)O_2 and *y* subcycles of ZrO_2 may be repeated to obtain a desired thickness of (Zr, Ge)O_2 film, wherein x and y are integers which inclusively range from 1 to 20. Zr and Ge content may be controlled by adjusting *x* and *y*.

Alternatively, the germanium content in the ZrO_2 film may be controlled by depositing the (Zr, Ge)O_2 film using a mixture containing both the disclosed Zirconium-containing film forming compositions and a zirconium-containing precursor. For example, $ZrCp(NMe_2)_3$, $Zr(MeCp)(NMe_2)_3$, $Zr(EtCp)(NMe_2)_3$, $Zr(iPrCp)(NMe_2)_3$, or $Zr(tBuCp)(NMe_2)_3$ may serve as the Zr-containing precursor. The Zr and Ge content may be controlled by adjusting the ratio between the Zirconium-containing film forming composition and the zirconium-containing precursor in the mixture.

The disclosed Zirconium-containing film forming compositions may be supplied either in neat form or in a blend with a suitable solvent, such as ethyl benzene, xylene, mesitylene, decane, or dodecane. The disclosed compositions may be present in varying concentrations in the solvent.

The neat or blended Zirconium-containing film forming compositions are introduced into a reactor in vapor form by conventional means, such as tubing and/or flow meters. The composition in vapor form may be produced by vaporizing the neat or blended composition through a conventional vaporization step such as direct vaporization, distillation, direct liquid injection, by bubbling, or by using a sublimator such as the one disclosed in PCT Publication WO2009/087609 to Xu et al. The neat or blended composition may be fed in liquid state to a vaporizer where it is vaporized before it is introduced into the reactor. Alternatively, the neat or blended composition may be vaporized by passing a carrier gas into a container containing the composition or by bubbling the carrier gas into the composition. The carrier gas may include, but is not limited to, Ar, He, N_2,and mixtures thereof. Bubbling with a carrier gas may also remove any dissolved oxygen present in the neat or blended composition. The carrier gas and composition are then introduced into the reactor as a vapor.

If necessary, the container of disclosed composition may be heated to a temperature that permits the composition to be in its liquid phase and to have a sufficient vapor pressure. The container may be maintained at temperatures in the range of, for example, approximately 0°C to approximately 150°C. Those skilled in the art recognize that the temperature of the container may be adjusted in a known manner to control the amount of composition vaporized.

The reactor may be any enclosure or chamber within a device in which deposition methods take place such as without limitation, a parallel-plate type reactor, a cold-wall type reactor, a hot-wall type reactor, a single-wafer reactor, a multi-wafer reactor (i.e., a batch reactor), or other types of deposition systems under conditions suitable to cause the precursors to react and form the layers.

Generally, the reactor contains the substrate(s) onto which the thin films will be deposited. A substrate is generally defined as the material on which a process is conducted. The substrates may be any suitable substrate used in semiconductor, photovoltaic, flat panel, or LCD-TFT device manufacturing. Examples of suitable substrates include wafers, such as silicon, silica, glass, or GaAs wafers. The wafer may have one or more layers of differing materials deposited on it from a previous manufacturing step. For example, the wafers may include silicon layers (crystalline, amorphous, porous, etc.), silicon oxide layers, silicon nitride layers, silicon oxy nitride layers, carbon doped silicon oxide (SiCOH) layers, or combination thereof. Additionally, the wafers may include copper layers, tungsten layers, or noble metal layers (e.g., platinum, palladium rhodium, or gold). Plastic layers, such as poly(3,4-ethylenedioxythiophene)poly (styrenesulfonate) [PEDOT:PSS], may also be used. The layers may be planar or patterned.

The disclosed processes may deposit the Zr-containing layer directly on the wafer or directly on one or more than one (when patterned layers from the substrate) of the layers on top of the wafer. The substrate may be patterned to include vias or trenches having high aspect ratios. For example, a conformal Zr-containing film, such as ZrO_2, may be deposited using any ALD technique on a through silicon via (TSV) having an aspect ratio ranging from approximately 20:1 to approximately 100:1. Furthermore, one of ordinary skill in the art will recognize that the terms "film" or "layer" used herein refer to a thickness of some material laid on or spread over a surface and that the surface may be a trench or a line.

Throughout the specification and claims, the wafer and any associated layers thereon are referred to as substrates. For example, a ZrO_2 film may be deposited onto a TiN substrate. In subsequent processing, a TiN layer may be deposited on the ZrO_2 layer, forming a TiN/ZrO_2/TiN stack used as DRAM capacitor.

The temperature and the pressure within the reactor are held at conditions suitable for vapor depositions. In other words, after introduction of the vaporized composition into the chamber, conditions within the chamber are such that at least part of the precursor is deposited onto the substrate to form a Zirconium-containing film. For instance, the pressure in the reactor may be held between about 1 Pa and about 10^5 Pa, more preferably between about 25 Pa and about 10^3 Pa, as required per the deposition parameters. Likewise, the temperature in the reactor may be held between about 100°C and about 500°C, preferably between about 150°C and about 400°C. One of ordinary skill in the art will recognize that "at least part of the precursor is deposited" means that some or all of the precursor in the disclosed Zr-containing film forming composition reacts with or adheres to the substrate, either by itself or with the aid of a reactant.

The temperature of the reactor may be controlled by either controlling the temperature of the substrate holder or controlling the temperature of the reactor wall. Devices used to heat the substrate are known in the art. The reactor wall is heated to a sufficient temperature to obtain the desired film at a sufficient growth rate and with desired physical state and composition. A non-limiting exemplary temperature range to which the reactor wall may be heated includes from approximately 100°C to approximately 500°C. When a plasma deposition process is utilized, the deposition temperature may range from approximately 150°C to approximately 400°C. Alternatively, when a thermal process is performed, the deposition temperature may range from approximately 200°C to approximately 500°C.

In addition to the disclosed Zr-containing film forming composition, a reactant may also be introduced into the reactor. The reactant may be an oxidizing gas such as one of O_2, O_3, H_2O, H_2O_2, NO, N_2O, NO_2, oxygen-containing radicals such as $O^\cdot$ or $OH^\cdot$, NO, NO_2,carboxylic acids, formic acid, acetic acid, propionic acid, and mixtures thereof. O_2 may include $^1\Delta_g$ singlet oxygen, $^1\Sigma_g^+$ singlet oxygen, the conventional $^3\Sigma_g^-$ triplet oxygen, or combinations thereof. The higher energy states of O_2 may be generated using electric discharge, irradiation of a photosensitizer such as that disclosed by Ito et al. in JP2012/087025, or by a MEMS chip, such as the one disclosed by Velásquez-García et al. (J Microelectromechanical Systems Vol. 16, No. 6, December 2007). Applicants believe that a mixture of singlet oxygen with triplet oxygen and/or ozone may provide suitable reactivity without damaging the underlying substrate due to the short lifespan of the higher energy state O_2. Alternatively, the oxidizing gas may be selected from the group consisting of O_2, O_3, H_2O, H_2O_2, oxygen-containing radicals thereof such as $O^{\cdot}$ or $OH^{\cdot}$, and mixtures thereof.

Alternatively, the reactant may be a reducing gas such as one of H_2, H_2CO, NH_3, SiH_4, Si_2H_6, Si_3H_8, $(CH_3)_2SiH_2$, $(C_2H_5)_2SiH_2$, $(CH_3)SiH_3$, $(C_2H_5)SiH_3$, phenyl silane, N_2H_4, $N(SiH_3)_3$, $N(CH_3)H_2$, $N(C_2H_5)H_2$, $N(CH_3)_2H$, $N(C_2H_5)_2H$, $N(CH_3)_3$, $N(C_2H_5)_3$, $(SiMe_3)_2NH$, $(CH_3)HNNH_2$, $(CH_3)_2NNH_2$, phenyl hydrazine, N-containing molecules, B_2H_6, 9-borabicyclo[3,3,1]nonane, dihydrobenzenfuran, pyrazoline, trimethylaluminium, dimethylzinc, diethylzinc, radical species thereof, and mixtures thereof. Preferably, the reducing gas is H_2, NH_3, SiH_4, Si_2H_6, Si_3H_8, SiH_2Me_2, SiH_2Et_2, $N(SiH_3)_3$, hydrogen radicals thereof, or mixtures thereof.

The reactant may be treated by plasma, in order to decompose the reactant into its radical form. N_2 may also be utilized as a reducing gas when treated with plasma. For instance, the plasma may be generated with a power ranging from about 50 W to about 500 W, preferably from about 100 W to about 400 W. The plasma may be generated or present within the reactor itself. Alternatively, the plasma may generally be at a location removed from the reactor, for instance, in a remotely located plasma system. One of skill in the art will recognize methods and apparatus suitable for such plasma treatment.

For example, the reactant may be introduced into a direct plasma reactor, which generates plasma in the reaction chamber, to produce the plasma-treated reactant in the reaction chamber. Exemplary direct plasma reactors include the Titan™ PECVD System produced by Trion Technologies. The reactant may be introduced and held in the reaction chamber prior to plasma processing. Alternatively, the plasma processing may occur simultaneously with the introduction of the reactant. In-situ plasma is typically a 13.56 MHz RF inductively coupled plasma that is generated between the showerhead and the substrate holder. The substrate or the showerhead may be the powered electrode depending on whether positive ion impact occurs. Typical applied powers in in-situ plasma generators are from approximately 30 W to approximately 1000 W. Preferably, powers from approximately 30 W to approximately 600 W are used in the disclosed methods. More preferably, the powers range from approximately 100 W to approximately 500 W. The disassociation of the reactant using in-situ plasma is typically less than achieved using a remote plasma source for the same power input and is therefore not as efficient in reactant disassociation as a remote plasma system, which may be beneficial for the deposition of Zirconium-containing films on substrates easily damaged by plasma.

Alternatively, the plasma-treated reactant may be produced outside of the reaction chamber. The MKS Instruments' ASTRONi® reactive gas generator may be used to treat the reactant prior to passage into the reaction chamber. Operated at 2.45 GHz, 7kW plasma power, and a pressure ranging from approximately 0.5 Torr to approximately 10 Torr, the reactant O_2 may be decomposed into two $O^{\cdot}$ radicals. Preferably, the remote plasma may be generated with a power ranging from about 1 kW to about 10 kW, more preferably from about 2.5 kW to about 7.5 kW.

The vapor deposition conditions within the chamber allow the disclosed precursors and the reactant to react and form a Zirconium-containing film on the substrate. In some embodiments, Applicants believe that plasma-treating the reactant may provide the reactant with the energy needed to react with the disclosed precursor.

Depending on what type of film is desired to be deposited, an additional precursor compound may be introduced into the reactor. The additional precursor may be used to provide the same (i.e., Zr) or additional elements to the Zirconium-containing film. The additional elements may include Hafnium, Niobium, Tantalum, lanthanides (Ytterbium, Erbium, Dysprosium, Gadolinium, Praseodymium, Cerium, Lanthanum, Yttrium), germanium, silicon, titanium, manganese, cobalt, nickel, ruthenium, bismuth, lead, magnesium, aluminum, or mixtures of these. When an additional precursor compound is utilized, the resultant film deposited on the substrate may contain the Zirconium in combination with at least one additional element.

The Zirconium-containing film forming compositions and reactants may be introduced into the reactor either simultaneously (chemical vapor deposition), sequentially (atomic layer deposition), or different combinations thereof. The reactor may be purged with an inert gas between the introduction of the composition and the introduction of the reactant. Alternatively, the reactant and the composition may be mixed together to form a reactant/composition mixture, and then introduced to the reactor in mixture form. Another example is to introduce the reactant continuously and to introduce the Zirconium-containing film forming composition by pulse (pulsed chemical vapor deposition).

The vaporized composition and the reactant may be pulsed sequentially or simultaneously (*e.g.* pulsed CVD) into the reactor. Each pulse of composition may last for a time period ranging from about 0.01 seconds to about 10 seconds, alternatively from about 0.3 seconds to about 3 seconds, alternatively from about 0.5 seconds to about 2 seconds. In another embodiment, the reactant may also be pulsed into the reactor. In such embodiments, the pulse of each gas may last for a time period ranging from about 0.01 seconds to about 10 seconds, alternatively from about 0.3 seconds to about 3 seconds, alternatively from about 0.5 seconds to about 2 seconds. In another alternative, the vaporized composition and one or more reactants may be simultaneously sprayed from a shower head under which a susceptor holding several wafers is spun (spatial ALD).

Depending on the particular process parameters, deposition may take place for a varying length of time. Generally, deposition may be allowed to continue as long as desired or necessary to produce a film with the necessary properties. Typical film thicknesses may vary from several angstroms to several hundreds of microns, depending on the specific deposition process. The deposition process may also be performed as many times as necessary to obtain the desired film thickness.

In one non-limiting exemplary CVD type process, the vapor phase of the disclosed Zirconium-containing film forming composition and a reactant are simultaneously introduced into the reactor. The two react to form the resulting Zirconium-containing thin film. When the reactant in this exemplary CVD process is treated with plasma, the exemplary CVD process becomes an exemplary

PECVD process. The reactant may be treated with plasma prior or subsequent to introduction into the chamber.

In one non-limiting exemplary ALD type process, the vapor phase of the disclosed Zirconium-containing film forming composition is introduced into the reactor, where it is contacted with a suitable substrate. Excess composition may then be removed from the reactor by purging and/or evacuating the reactor. A reactant (for example, H_2) is introduced into the reactor where it reacts with the physi- or chemi-sorbed precursor in a self-limiting manner. Any excess reactant is removed from the reactor by purging and/or evacuating the reactor. If the desired film is a Zirconium film, this two-step process may provide the desired film thickness or may be repeated until a film having the necessary thickness has been obtained.

Alternatively, if the desired film contains Zirconium and a second element, the two-step process above may be followed by introduction of the vapor of an additional precursor compound into the reactor. The additional precursor compound will be selected based on the nature of the Zirconium film being deposited. After introduction into the reactor, the additional precursor compound is contacted with the substrate. Any excess precursor compound is removed from the reactor by purging and/or evacuating the reactor. Once again, a reactant may be introduced into the reactor to react with the physi- or chemi-sorbed precursor compound. Excess reactant gas is removed from the reactor by purging and/or evacuating the reactor. If a desired film thickness has been achieved, the process may be terminated. However, if a thicker film is desired, the entire four-step process may be repeated. By alternating the provision of the Zirconium-containing film forming composition, additional precursor compound, and reactant, a film of desired composition and thickness can be deposited.

When the reactant in this exemplary ALD process is treated with plasma, the exemplary ALD process becomes an exemplary PEALD process. The reactant may be treated with plasma prior or subsequent to introduction into the chamber.

In a second non-limiting exemplary ALD type process, the vapor phase of one of the disclosed Zr-containing film forming compositions, for example (trimethylgermyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV), is introduced into the reactor, where it is contacted with a TiN substrate. Excess Zr-containing film forming composition may then be removed from the reactor by purging and/or evacuating the reactor. A reactant (for example, O_3) is introduced into the reactor where it reacts with the physi- or chemi-sorbed precursor in a self-limiting manner to form a ZrO_2 or (Zr, Ge)O_2 film. Any excess reactant is removed from the reactor by purging and/or evacuating the reactor. These two steps may be repeated until the ZrO_2 or (Zr, Ge)O_2 film obtains a desired thickness. A TiN layer may then be deposited on top of the ZrO_2 or (Zr, Ge)O_2 layer. The resulting TiN/ZrO_2/TiN or TiN/(Zr, Ge)O_2/TiN stack may be used in DRAM capacitors.

In a third non-limiting exemplary ALD type process, the vapor phase of one of the disclosed Zr-containing film forming compositions, for example (trimethylgermyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV), is introduced in a first step into the reactor, where it is contacted with a TiN substrate. Excess Zr-containing film forming composition may then be removed from the reactor by purging and/or evacuating the reactor. A reactant (for example, O_3) is introduced into the reactor where it reacts with the physi- or chemi-sorbed precursor in a self-limiting manner to form a (Zr, Ge)O_2 film. Any excess reactant is removed from the reactor by purging and/or evacuating the reactor. These two steps may be considered as a subcycle and may be repeated *x* times to obtain a desired thickness of the (Zr, Ge)O_2 film.

In a second step the vapor phase of a Zr-containing precursor, for example (methyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV) or (ethyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV) is introduced into the same reactor. Excess Zr-containing precursor may then be removed from the reactor by purging and/or evacuating the reactor. A reactant (for example, O_3) is introduced into the reactor where it reacts with the physi- or chemi-sorbed Zr-containing precursor in a self-limiting manner to form a ZrO_2 film. Any excess reactant is removed from the reactor by purging and/or evacuating the reactor. These two steps may be considered as a subcycle and may be repeated *y* times to obtain a desired thickness of ZrO_2 film.

The supercycle consisting of x subcycles of (Zr, Ge)O_2 and y subcycles of ZrO_2 may be be repeated to obtain a desired thickness of (Zr, Ge)O_2 film. Zr and Ge content may be controlled by adjusting the number of x and y cycles (x and y may independently range from 1 to 20). A TiN layer may then be deposited on top of the ZrO_2 or (Zr, Ge)O_2 layer. The resulting TiN/ZrO_2/TiN or TiN/(Zr, Ge)O_2/TiN stack may be used in DRAM capacitors.

In a fourth non-limiting exemplary ALD type process, the vapor phase of a mixture containing the disclosed Zr-containing film forming composition, for example (trimethylgermyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV), and a Zr-containing precursor, for example (isopropyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV) or (tertbutyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV), is introduced into the reactor, where it is contacted with a substrate, for example TiN, NbN, Ru, TiO_2, MoO_2 or MoO_3. Excess mixture may then be removed from the reactor by purging and/or evacuating the reactor. A reactant (for example, O_3) is introduced into the reactor where it reacts with the physi- or chemi-sorbed precursors in a self-limiting manner to form a (Zr, Ge)O_2 film. Any excess reactant is removed from the reactor by purging and/or evacuating the reactor. These two steps may be repeated until the (Zr, Ge)O_2 film obtains a desired thickness. The Zr and Ge content may be controlled by adjusting the ratio between the Zirconium-containing film forming composition and the zirconium-containing precursor in the mixture. A TiN layer may be deposited on top of the (Zr, Ge)O_2 layer. The resulting TiN/ZrO_2/TiN or TiN/(Zr, Ge)O_2/TiN stack may be used in DRAM capacitors.

The Zirconium-containing films resulting from the processes discussed above may include a pure Zirconium, Zirconium silicide (Zr_kSi_l), Zirconium oxide (Zr_mO_n), Germanium-doped Zirconium oxide ($Zr_rGe_sO_t$), Zirconium nitride (Zr_uN_v), or germanium-doped silicon nitride ($Zr_tGe_uN_v$), wherein k, l, m, n, o, p, q, r, s, t, u and v are integers which inclusively range from 1 to 6. One of ordinary skill in the art will recognize that by judicial selection of the appropriate disclosed Zr-containing film forming composition, optional precursor compounds, and reactant species, the desired film composition may be obtained.

Upon obtaining a desired film thickness, the film may be subject to further processing, such as thermal annealing, furnace-annealing, rapid thermal annealing, UV or e-beam curing, and/or plasma gas exposure. Those skilled in the art recognize the systems and methods utilized to perform these additional processing steps. For example, the Zirconium-containing film may be exposed to a temperature ranging from approximately 200°C and approximately 1000°C for a time ranging from approximately 0.1 second to approximately 7200 seconds under an inert atmosphere, a H-containing atmosphere, a N-containing atmosphere, an O-containing atmosphere, or combinations thereof. Most preferably, the temperature is 400°C for 3600 seconds under a H-containing atmosphere or an O-containing atmosphere. The resulting film may contain fewer impurities and therefore may have an improved density resulting in improved leakage current. The annealing step may be performed in the same reaction chamber in which the deposition process is performed. Alternatively, the substrate may be removed from the reaction chamber, with the annealing/flash annealing process being performed in a separate apparatus. Any of the above post-treatment methods, but especially thermal annealing, has been found effective to reduce carbon and nitrogen contamination of the Zirconium-containing film. This in turn tends to improve the resistivity of the film.

Examples

The following examples illustrate experiments performed in conjunction with the disclosure herein. The examples are not intended to be all inclusive and are not intended to limit the scope of disclosure described herein.

<u>Example 1</u>: (trimethylgermyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV) synthesis [$Zr(TMG\text{-}Cp)(NMe_2)_3$]

To a solution of $Zr(NMe_2)_4$ (1.33 g, 0.005 mol) in *ca.* 20 mL of toluene at room temperature, was added dropwise a freshly distilled TMGCpH (0.93 g, 0.005 mol). The mixture was stirred overnight. Solvent was then removed under vacuum to give yellow oil. The material was then purified by distillation at 120 °C @ 6 mTorr to give 1.38 g (68%) of pure yellow oil. The NMR^1H spectrum is provided in **FIG 3**. NMR^1H (δ, ppm, C6D6): 6.28 (t, 2H), 6.23 (t, 2H), 2.95 (s, 18H), 0.38 (s, 9H).

The oil left a 3.9% residual mass during TGA analysis measured at a temperature rising rate of 10°C/min in an atmosphere which flows nitrogen at 200 mL/min. These results are shown in **FIG 5**, which is a TGA/DTA graph illustrating the percentage of weight loss (TGA) and differential temperature (DTA) upon temperature increase. Decomposition occurs at approximately 285°C. Volatility is 127°C at 1 Torr.

Example 2: (trimethylgermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) synthesis [Zr(TMG-Cp)(OiPr)$_3$]

To a solution of Zr(TMGCp)(NMe$_2$)$_3$ (1.26 g, 2.8 mmol) in *ca.* 20 mL of THF, was added drop wise anhydrous isopropanol (0.63 g, 10.5 mmol). The mixture was stirred overnight at room temperature. Solvent was then removed under vacuum to give bright yellow oil. The material was then purified by distillation at 90 °C @ 20 mTorr to give 0.39 g (31%) of pure slightly yellow oil. The NMR^{1}H spectrum is provided in **FIG 4**. NMR^{1}H (δ, ppm, C6D6): 6.56 (t, 2H), 6.43 (t, 2H), 4.25 (m, 3H), 1.17 (d, 18H), 0.48 (s, 9H).

The oil left a 1.6% residual mass during TGA analysis measured at a temperature rising rate of 10°C/min in an atmosphere which flows nitrogen at 200 mL/min. These results are shown in **FIG 6**, which is a TGA/DTA graph illustrating the percentage of weight loss (TGA) and differential temperature (DTA) upon temperature increase. Decomposition occurs at approximately 385°C. Volatility is 104°C at 1 Torr.

Example 3: Atomic Layer Deposition of Zirconium Germanium Oxide from Zr(TMG-Cp)(NMe$_2$)$_3$ and O$_3$

ALD tests were performed using the Zr(TMG-Cp)(NMe$_2$)$_3$ prepared similarly to that of Example 1, which was be placed in a vessel heated to 80ºC and O$_3$ as oxidizing reactant. Typical ALD conditions were used with a reactor pressure fixed at ~0.5 Torr. ALD behavior with complete surface saturation and reaction was assessed in a temperature window of 250-425ºC on silicon wafers. The growth rates in ALD window of 250-350ºC were in the range 0.35 - 0.50 Å/cycle. **FIG 7** shows the growth rates of ZrO$_2$ thin films using Zr(TMG-Cp)(NMe$_2$)$_3$/O$_3$ as a function of the temperature. **FIG 8** shows the X-ray Photoelectron Spectroscopy (XPS) of the resulting ZrO$_2$ films and shows that all impurities are below the detection limit of the analytic tool (<1%).

Fig 9 shows the Scanning Electron Microscope (SEM) of the film deposited in a 1:10 aspect ratio pattern wafer using (trimethylgermyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV) at 325°C and shows 100% step coverage performance. **Fig 10** also shows the SEM of the film deposited in a 1:40 aspect ratio pattern wafer using (trimethylgermyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV) at 325°C and shows 100% step coverage performance.

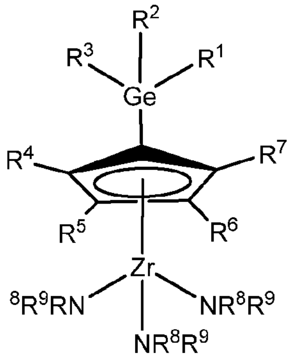
<u>Example 4</u>: Atomic Layer Deposition of Zirconium Germanium Oxide from Zr(TMG-Cp)$(NMe_2)_3$ and H_2O

ALD tests were performed using the Zr(TMG-Cp)$(NMe_2)_3$ prepared similarly to that of Example 1, which was be placed in a vessel heated to 80°C and O_3 as oxidizing reactant. Typical ALD conditions were used with a reactor pressure fixed at ~0.5 Torr. ALD behavior with complete surface saturation and reaction was assessed in a temperature window of 250-375°C on silicon wafers. The growth rates in ALD window of 250-375°C was 0.50 Å/cycle. **FIG 11** shows the growth rates of ZrO_2 thin films using Zr(TMG-Cp)$(NMe_2)_3$/H_2O as a function of the temperature. **FIG 12** shows the X-ray Photoelectron Spectroscopy (XPS) of the resulting $ZrGeO_2$ film grown at 300°C and shows that all impurities are below the detection limit of the analytic tool (<1%).

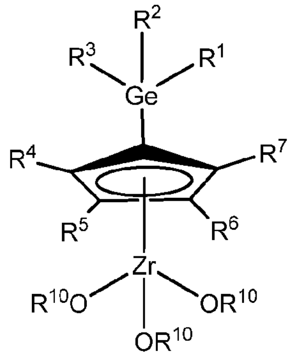
It will be understood that many additional changes in the details, materials, steps, and arrangement of parts, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims. Thus, the present invention is not intended to be limited to the specific embodiments in the examples given above and/or the attached drawings.

We claim:

1. A Zirconium-containing film forming composition comprising a Germanium- and Zirconium-containing precursor having one of the following formulae:



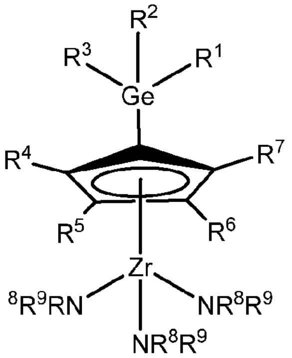
Formula I



Formula II

wherein each R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} is independently selected from the group consisting of H; a C1-C5 linear, branched, or cyclic alkyl group; and a C1-C5 linear, branched, or cyclic fluoroalkyl group.

2. The Zirconium-containing film forming composition of claim 1, the precursor having the Formula I:



Formula I

3. The Zirconium-containing film forming composition of claim 2, wherein the precursor is selected from the group consisting of: (trimethylgermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) (Zr(TMG-Cp)(NMe_2)$_3$); (trimethylgermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) (Zr(TMG-Cp)(NHMe)$_3$); (trimethylgermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) (Zr(TMG-Cp)(NEt_2)$_3$); (trimethylgermyl)cyclopentadienyl

tris(ethylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHEt)_3$); (trimethylgermyl)cyclopentadienyl tris(ethylmethylamino) Zirconium(IV) ($Zr(TMG-Cp)(NEtMe)_3$); (trimethylgermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr(TMG-Cp)(NnPr_2)_3$); (trimethylgermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHnPr)_3$); (trimethylgermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr(TMG-Cp)(NiPr_2)_3$); (trimethylgermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHiPr)_3$); (trimethylgermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NnBu_2)_3$); (trimethylgermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHnBu)_3$) (trimethylgermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr(TMG-Cp)(NiBu_2)_3$); (trimethylgermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHiBu)_3$); (trimethylgermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NsBu_2)_3$); (trimethylgermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHsBu)_3$); (trimethylgermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NtBu_2)_3$); (trimethylgermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr(TMG-Cp)(NHtBu)_3$); (dimethylgermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr(DMG-Cp)(NMe_2)_3$); (dimethylgermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHMe)_3$); (dimethylgermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr(DMG-Cp)(NEt_2)_3$); (dimethylgermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHEt)_3$); (dimethylgermyl)cyclopentadienyl tris(ethylmethylamino) Zirconium(IV) ($Zr(DMG-Cp)(NEtMe)_3$); (dimethylgermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr(DMG-Cp)(NnPr_2)_3$); (dimethylgermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHnPr)_3$); (dimethylgermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr(DMG-Cp)(NiPr_2)_3$); (dimethylgermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHiPr)_3$); (dimethylgermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr(DMG-Cp)(NnBu_2)_3$); (dimethylgermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHnBu)_3$); (dimethylgermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr(DMG-Cp)(NiBu_2)_3$); (dimethylgermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHiBu)_3$); (dimethylgermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr(DMG-Cp)(NsBu_2)_3$); (dimethylgermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHsBu)_3$); (dimethylgermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr(DMG-Cp)(NtBu_2)_3$); (dimethylgermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr(DMG-Cp)(NHtBu)_3$); (trifluorogermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NMe_2)_3$); (trifluorogermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NHMe)_3$); (trifluorogermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NEt_2)_3$); (trifluorogermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NHEt)_3$); (trifluorogermyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NEtMe)_3$); (trifluorogermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NnPr_2)_3$); (trifluorogermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NHnPr)_3$) (trifluorogermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NiPr_2)_3$); (trifluorogermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NHiPr)_3$); (trifluorogermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NnBu_2)_3$); (trifluorogermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NHnBu)_3$); (trifluorogermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NiBu_2)_3$); (trifluorogermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NHiBu)_3$); (trifluorogermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NsBu_2)_3$); (trifluorogermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NHsBu)_3$); (trifluorogermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NtBu_2)_3$); (trifluorogermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr(F_3Ge-Cp)(NHtBu)_3$); (difluorogermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NMe_2)_3$); (difluorogermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NHMe)_3$); (difluorogermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NEt_2)_3$); (difluorogermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NHEt)_3$); (difluorogermyl)cyclopentadienyl tris(Ethylmethylamino)

Zirconium(IV) ($Zr(F_2HGe-Cp)(NEtMe)_3$); (difluorogermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NnPr_2)_3$); (difluorogermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NHnPr)_3$); (difluorogermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NiPr_2)_3$); (difluorogermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NHiPr)_3$); (difluorogermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NnBu_2)_3$); (difluorogermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NHnBu)_3$); (difluorogermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NiBu_2)_3$); (difluorogermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NHiBu)_3$); (difluorogermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NsBu_2)_3$); (difluorogermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NHsBu)_3$); (difluorogermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NtBu_2)_3$); (difluorogermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr(F_2HGe-Cp)(NHtBu)_3$); (monofluorogermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NMe_2)_3$); (monofluorogermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHMe)_3$); (monofluorogermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NEt_2)_3$); (monofluorogermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHEt)_3$); (monofluorogermyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NEtMe)_3$); (monofluorogermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NnPr_2)_3$); (monofluorogermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHnPr)_3$); (monofluorogermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NiPr_2)_3$); (monofluorogermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHiPr)_3$); (monofluorogermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NnBu_2)_3$); (monofluorogermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NHnBu)_3$); (monofluorogermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr(FH_2Ge-Cp)(NiBu_2)_3$) (monofluorogermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) (Zr(FH$_2$Ge-

Cp)($NHiBu)_3$); (monofluorogermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) (Zr(FH_2Ge-Cp)($NsBu_2)_3$); (monofluorogermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) (Zr(FH_2Ge-Cp)($NHsBu)_3$); (monofluorogermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) (Zr(FH_2Ge-Cp)($NtBu_2)_3$); (monofluorogermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) (Zr(FH_2Ge-Cp)($NHtBu)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NMe_2)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NHMe)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NEt_2)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NHEt)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NEtMe)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NnPr_2)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NHnPr)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NiPr_2)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NHiPr)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NnBu_2)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NHnBu)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NiBu_2)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NHiBu)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NsBu_2)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NHsBu)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NtBu_2)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) (Zr(FMe_2Ge-Cp)($NHtBu)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) (Zr($(CF_3)_3Ge$-Cp)($NMe_2)_3$);

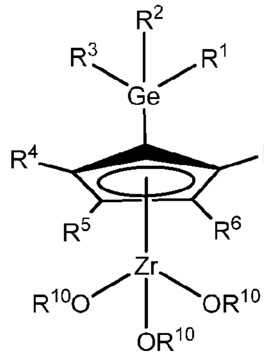
(tris(trifluoromethyl)germyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NHMe)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NEt_2)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NHEt)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NEtMe)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NnPr_2)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NHnPr)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NiPr_2)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NHiPr)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NnBu_2)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NHnBu)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NiBu_2)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NHiBu)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NsBu_2)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NHsBu)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NtBu_2)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr((CF_3)_3Ge-Cp)(NHtBu)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NMe_2)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHMe)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NEt_2)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(ethylamino) Zirconium(IV)

($Zr((CF_3)_2HGe-Cp)(NHEt)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NEtMe)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NnPr_2)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHnPr)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NiPr_2)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHiPr)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NnBu_2)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHnBu)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NiBu_2)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHiBu)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NsBu_2)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHsBu)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NtBu_2)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr((CF_3)_2HGe-Cp)(NHtBu)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Dimethylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge-Cp)(NMe_2)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(methylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge-Cp)(NHMe)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Diethylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge-Cp)(NEt_2)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(ethylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge-Cp)(NHEt)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Ethylmethylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge-Cp)(NEtMe)_3$);

((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di n-propylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NnPr_2)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(n-propylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHnPr)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di isopropylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NiPr_2)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(isopropylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHiPr)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di n-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NnBu_2)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(n-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHnBu)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di isobutylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NiBu_2)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(isobutylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHiBu)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di sec-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NsBu_2)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(sec-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHsBu)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(Di tert-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NtBu_2)_3$); and ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(tert-butylamino) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(NHtBu)_3$).

4. The Zirconium-containing film forming composition of claim 3, wherein the precursor is (trimethylgermyl)cyclopentadienyl tris(dimethylamino) Zirconium(IV) [$Zr(TMG\text{-}Cp)(NMe_2)_3$].

5. The Zirconium-containing film forming composition of claim 1, the precursor having the Formula II:



Formula II.

6. The Zirconium-containing film forming composition of claim 5, wherein the precursor is selected from the group consisting of: (trimethylgermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) (Zr(TMG-Cp)(OMe)$_3$); (trimethylgermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) (Zr(TMG-Cp)(OEt)$_3$); (trimethylgermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) (Zr(TMG-Cp)(OnPr)$_3$); (trimethylgermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) (Zr(TMG-Cp)(OiPr)$_3$); (trimethylgermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) (Zr(TMG-Cp)(OtBu)$_3$); (trimethylgermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) (Zr(TMG-Cp)(OsBu)$_3$); (trimethylgermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) (Zr(TMG-Cp)(OnBu)$_3$); (trimethylgermyl)cyclopentadienyl tris(iso-butoxy) Zirconium(IV) (Zr(TMG-Cp)(OiBu)$_3$); (dimethylgermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) (Zr(DMG-Cp)(OMe)$_3$); (dimethylgermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) (Zr(DMG-Cp)(OEt)$_3$); (dimethylgermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) (Zr(DMG-Cp)(OnPr)$_3$); (dimethylgermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) (Zr(DMG-Cp)(OiPr)$_3$); (dimethylgermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) (Zr(DMG-Cp)(OtBu)$_3$); (dimethylgermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) (Zr(DMG-Cp)(OsBu)$_3$); (dimethylgermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) (Zr(DMG-Cp)(OnBu)$_3$); (dimethylgermyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) (Zr(DMG-Cp)(OiBu)$_3$); (trifluorogermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) (Zr(F$_3$Ge-Cp)(OMe)$_3$); (trifluorogermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) (Zr(F$_3$Ge-Cp)(OEt)$_3$); (trifluorogermyl)cyclopentadienyl tris(n-propoxy)

Zirconium(IV) ($Zr(F_3Ge-Cp)(OnPr)_3$); (trifluorogermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr(F_3Ge-Cp)(OiPr)_3$); (trifluorogermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr(F_3Ge-Cp)(OtBu)_3$); (trifluorogermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) ($Zr(F_3Ge-Cp)(OsBu)_3$); (trifluorogermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) ($Zr(F_3Ge-Cp)(OnBu)_3$); (trifluorogermyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) ($Zr(F_3Ge-Cp)(OiBu)_3$); (difluorogermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OMe)_3$); (difluorogermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OEt)_3$); (difluorogermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OnPr)_3$); (difluorogermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OiPr)_3$); (difluorogermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OtBu)_3$); (difluorogermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OsBu)_3$); (difluorogermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OnBu)_3$); (difluorogermyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) ($Zr(F_2HGe-Cp)(OiBu)_3$); (monofluorogermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) ($Zr(FH_2Ge-Cp)(OMe)_3$); (monofluorogermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) ($Zr(FH_2Ge-Cp)(OEt)_3$); (monofluorogermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) ($Zr(FH_2Ge-Cp)(OnPr)_3$); (monofluorogermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr(FH_2Ge-Cp)(OiPr)_3$); (monofluorogermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr(FH_2Ge-Cp)(OtBu)_3$); (monofluorogermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) ($Zr(FH_2Ge-Cp)(OsBu)_3$); (monofluorogermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) ($Zr(FH_2Ge-Cp)(OnBu)_3$); (monofluorogermyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) ($Zr(FH_2Ge-Cp)(OiBu)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(OMe)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(OEt)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(OnPr)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr(FMe_2Ge-Cp)(OiPr)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr(FMe_2Ge-$

Cp)$(OtBu)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) (Zr(FMe_2Ge-Cp)$(OsBu)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) (Zr(FMe_2Ge-Cp)$(OnBu)_3$); (fluoro dimethylgermyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) (Zr(FMe_2Ge-Cp)$(OiBu)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(methoxy) Zirconium(IV) (Zr($(CF_3)_3Ge$-Cp)$(OMe)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) (Zr($(CF_3)_3Ge$-Cp)$(OEt)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) (Zr($(CF_3)_3Ge$-Cp)$(OnPr)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) (Zr($(CF_3)_3Ge$-Cp)$(OiPr)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) (Zr($(CF_3)_3Ge$-Cp)$(OtBu)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) (Zr($(CF_3)_3Ge$-Cp)$(OsBu)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) (Zr($(CF_3)_3Ge$-Cp)$(OnBu)_3$); (tris(trifluoromethyl)germyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) (Zr($(CF_3)_3Ge$-Cp)$(OiBu)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(methoxy) Zirconium(IV) (Zr($(CF_3)_2HGe$-Cp)$(OMe)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) (Zr($(CF_3)_2HGe$-Cp)$(OEt)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) (Zr($(CF_3)_2HGe$-Cp)$(OnPr)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) (Zr($(CF_3)_2HGe$-Cp)$(OiPr)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) (Zr($(CF_3)_2HGe$-Cp)$(OtBu)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) (Zr($(CF_3)_2HGe$-Cp)$(OsBu)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) (Zr($(CF_3)_2HGe$-Cp)$(OnBu)_3$); (bis(trifluoromethyl)germyl)cyclopentadienyl tris(iso-butoxy) Zirconium(IV) (Zr($(CF_3)_2HGe$-Cp)$(OiBu)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(methoxy) Zirconium(IV) (Zr($(CF_3)Me_2Ge$-Cp)$(OMe)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(ethoxy) Zirconium(IV) (Zr($(CF_3)Me_2Ge$-Cp)$(OEt)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(n-propoxy) Zirconium(IV) (Zr($(CF_3)Me_2Ge$-Cp)$(OnPr)_3$);

((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OiPr)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(tert-butoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OtBu)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(sec-butoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OsBu)_3$); ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(n-butoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OnBu)_3$); and ((trifluoromethyl)dimethylgermyl)cyclopentadienyl tris(isobutoxy) Zirconium(IV) ($Zr((CF_3)Me_2Ge\text{-}Cp)(OiBu)_3$).

7. The Zirconium-containing film forming composition of claim 6, wherein the precursor is (trimethylgermyl)cyclopentadienyl tris(isopropoxy) Zirconium(IV) [$Zr(TMG\text{-}Cp)(OiPr)_3$].

8. The Zirconium-containing film forming composition of claim 1, the composition comprising between approximately 95% w/w and approximately 100% w/w of the precursor.

9. The Zirconium-containing film forming composition of claim 1, the composition comprising between approximately 0.0% w/w and approximately 5.0% w/w impurities.

10. The Zirconium-containing film forming composition of claim 9, the impurities including alcohol; alkylamines; dialkylamines; alkylimines; cyclopentadiene; dicyclopentadiene; alkylgermane; THF; ether; pentane; cyclohexane; heptane; benzene; toluene; chlorinated metal compounds; lithium, sodium, or potassium alkylamino; lithium, sodium, or potassium alkylakoxy; and/or lithium, sodium, or potassium cyclopentadienyl.

11. The Zirconium-containing film forming composition of claim 1, the composition comprising between approximately 0 ppbw and approximately 1 ppmw metal impurities.

12. The Zirconium-containing film forming composition of claim 11, the metal impurities including Aluminum (Al), Arsenic (As), Barium (Ba), Beryllium (Be), Bismuth (Bi), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Cobalt (Co), Copper (Cu), Gallium (Ga), Germanium (Ge), Hafnium (Hf), Zirconium (Zr), Indium (In), Iron (Fe), Lead (Pb), Lithium (Li), Magnesium (Mg), Manganese (Mn), Tungsten (W), Nickel (Ni), Potassium (K), Sodium (Na), Strontium (Sr), Thorium (Th), Tin (Sn), Titanium (Ti), Uranium (U), and/or Zinc (Zn).

13. A process for the deposition of a Zirconium-containing film on a substrate, the process comprising the steps of: introducing a vapor of the Zirconium-containing film forming composition of any one of claims 1 to 12 into a reactor having a substrate disposed therein and depositing at least part of the Germanium- and Zirconium-containing precursor onto the substrate.

14. The process of claim 13, further comprising introducing at least one reactant into the reactor, wherein the reactant is selected from the group consisting of H_2, H_2CO N_2H_4, NH_3, SiH_4, Si_2H_6, Si_3H_8, SiH_2Me_2, SiH_2Et_2, $N(SiH_3)_3$, hydrogen radicals thereof, and mixtures thereof.

15. The process of claim 13, further comprising introducing at least one reactant into the reactor, wherein the reactant is selected from the group consisting of: O_2, O_3, H_2O, H_2O_2 NO, N_2O, NO_2, oxygen radicals thereof, and mixtures thereof.

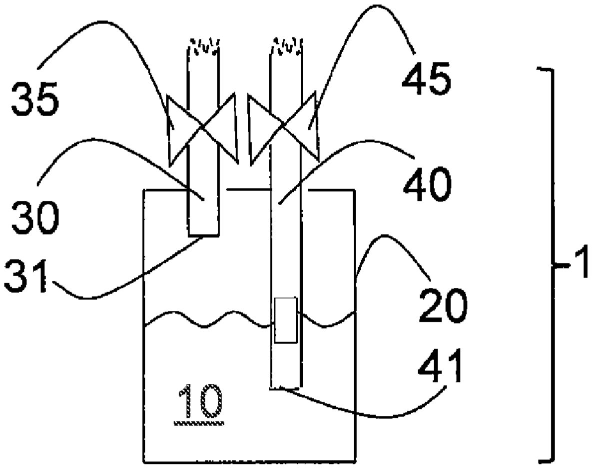


FIG 1

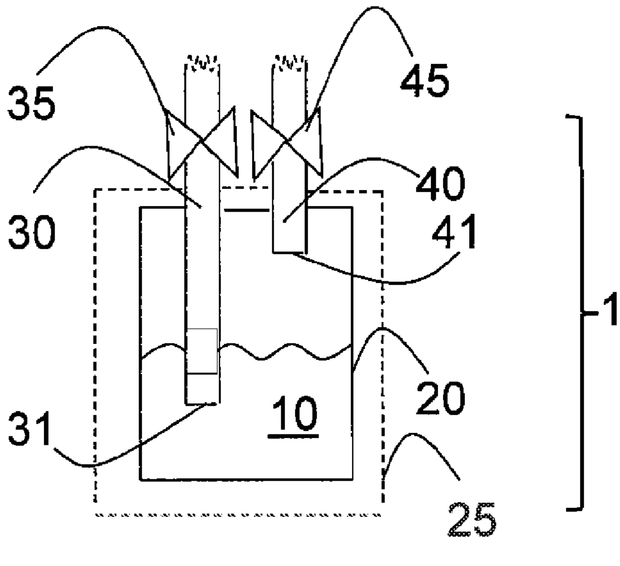


FIG 2

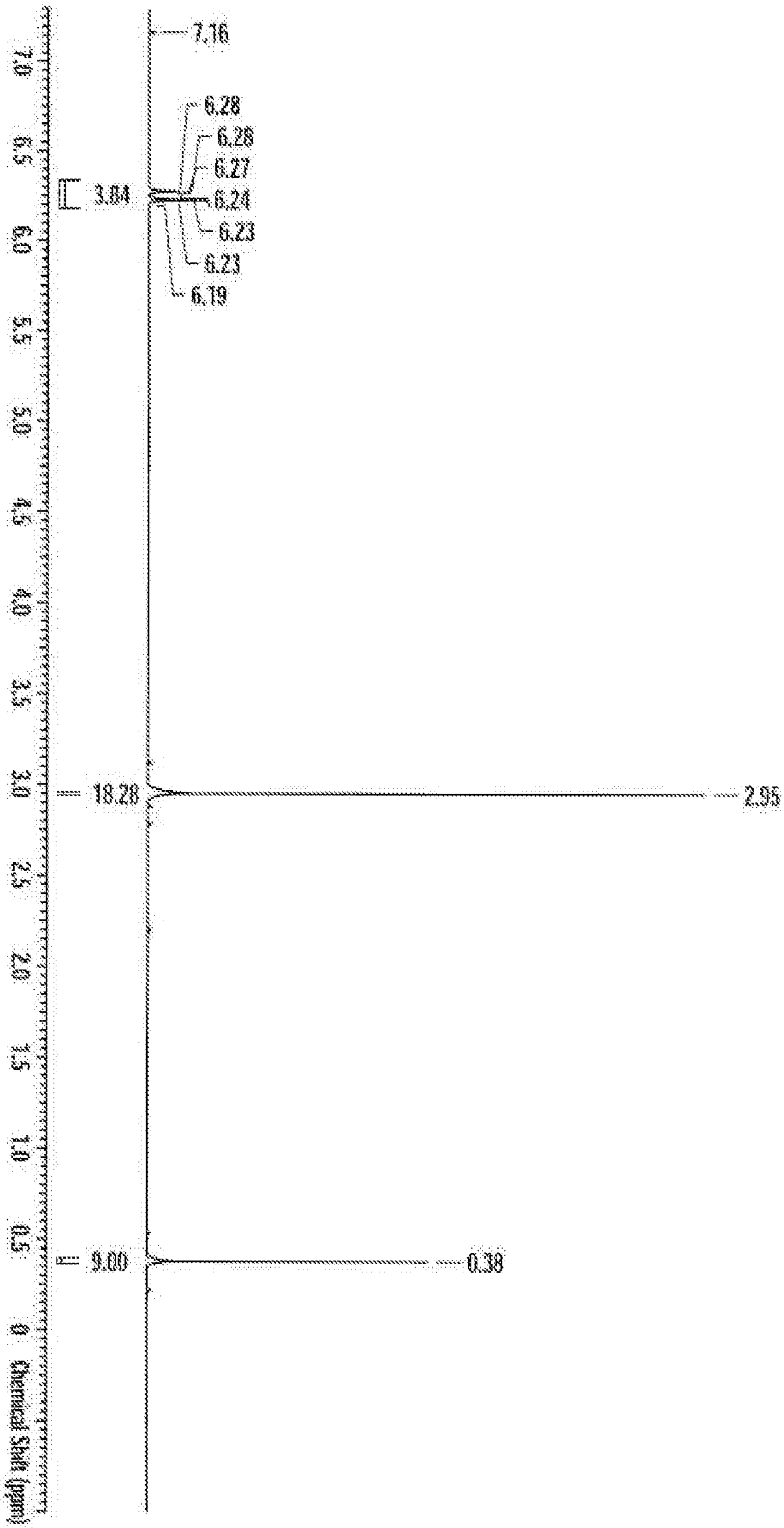

7.16
6.28
6.28
6.27
6.24
6.23
6.23
6.19
3.04
18.28
2.95
9.00
0.38
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

FIG. 3

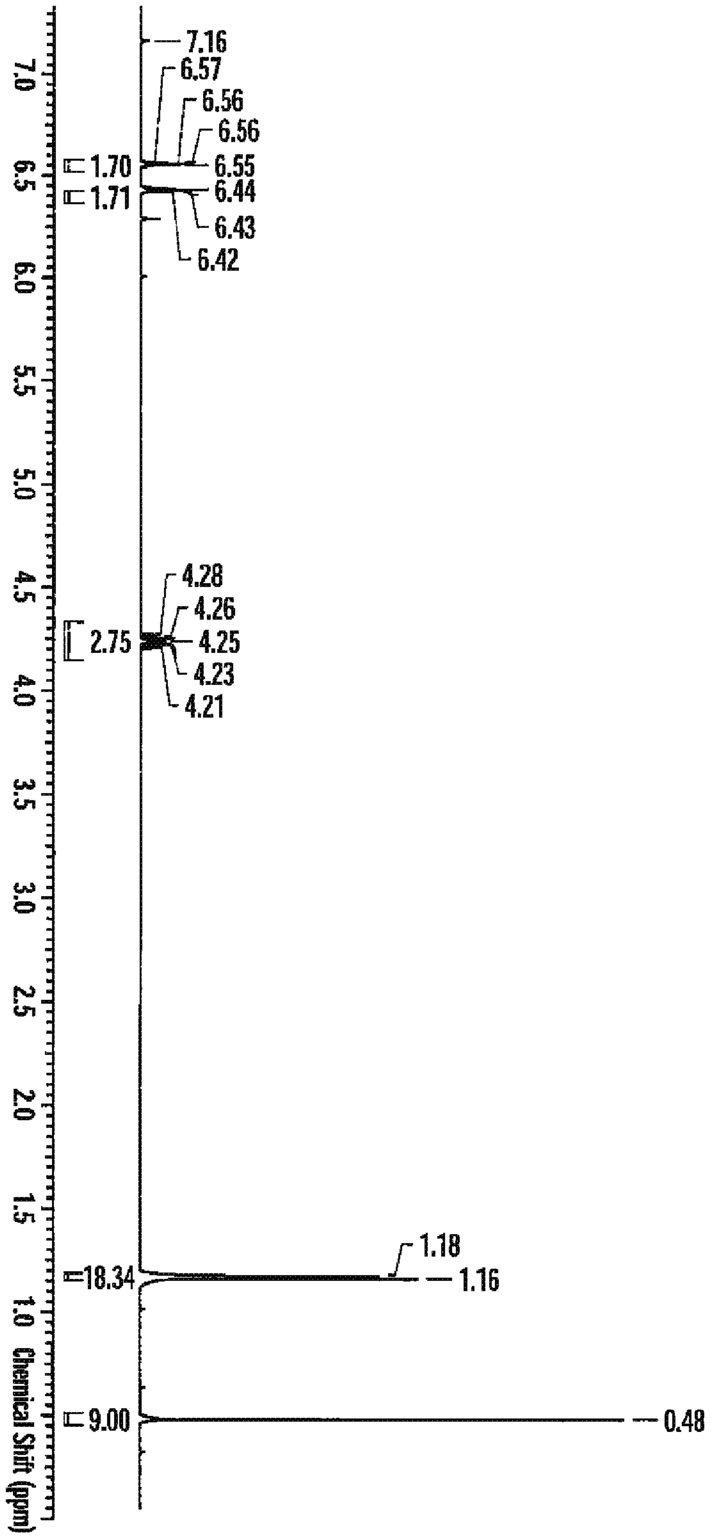
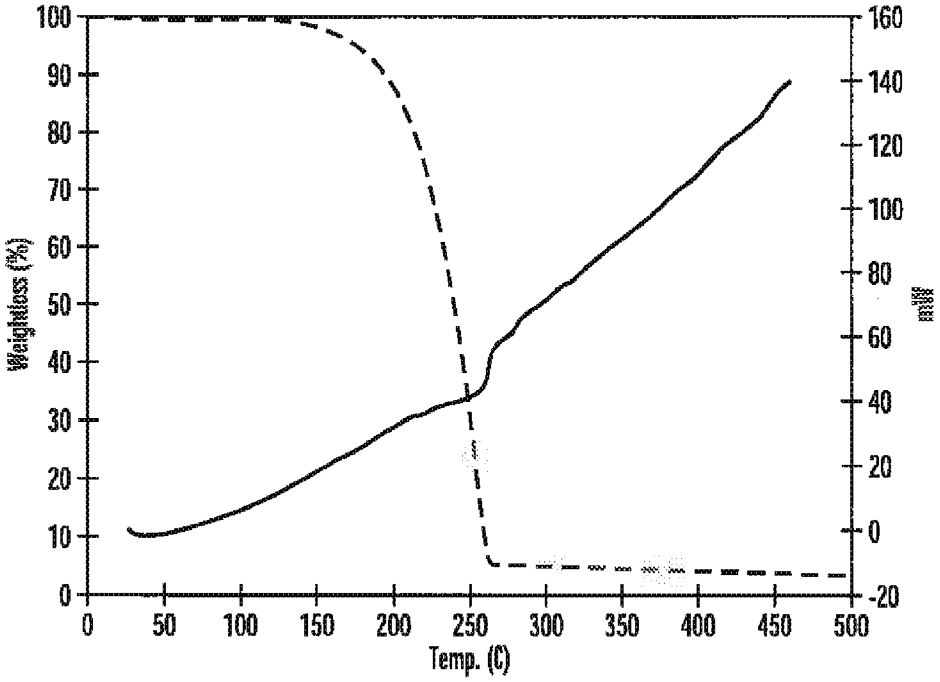
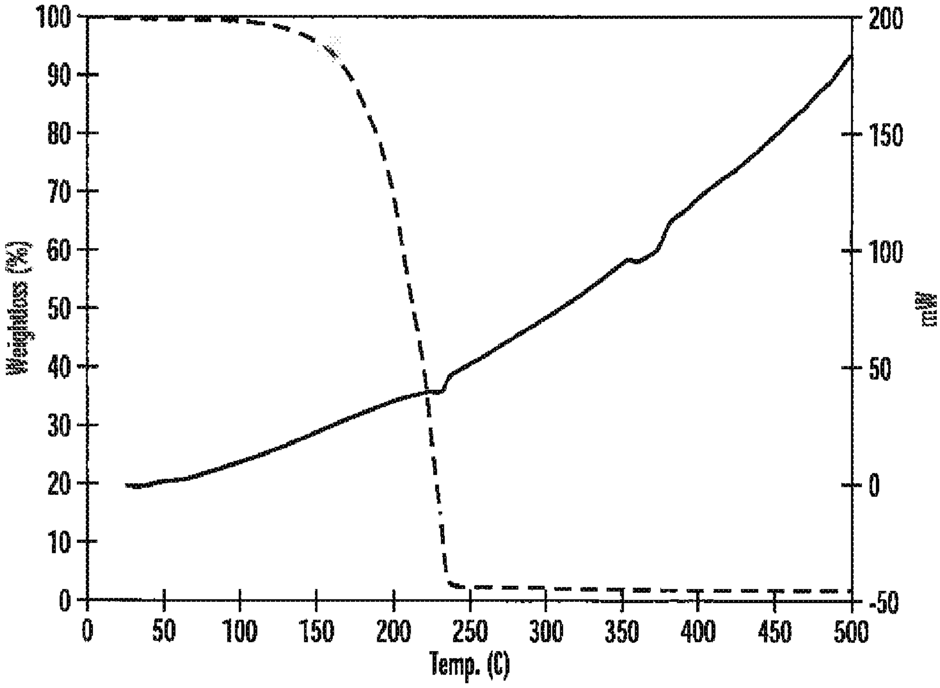

7.16
6.57
6.56
6.56
6.55
6.44
6.43
6.42
1.70
1.71
4.28
4.26
4.25
4.23
4.21
2.75
1.18
1.16
18.34
9.00
0.48
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

FIG. 4



100
90
80
70
60
50
40
30
20
10
0
Weightloss (%)
160
140
120
100
80
60
40
20
0
-20
mW
0
50
100
150
200
250
300
350
400
450
500
Temp. (C)

FIG. 5



100
90
80
70
60
50
40
30
20
10
0
Weightloss (%)
200
150
100
50
0
-50
mW
0
50
100
150
200
250
300
350
400
450
500
Temp. (C)

FIG. 6

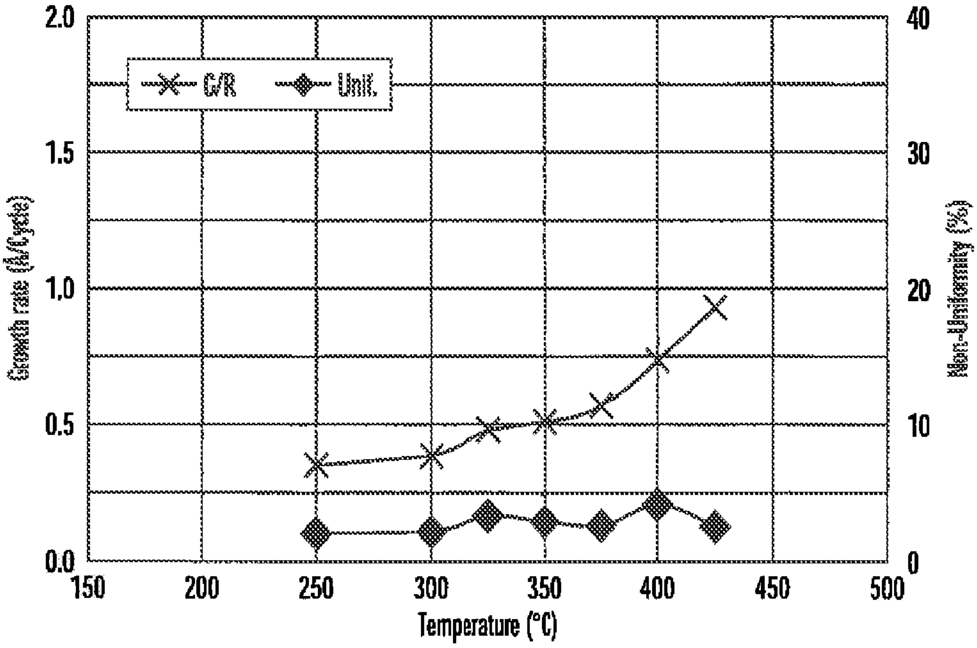

C/R
Unif.
Growth rate (Å/Cycle)
Non-Uniformity (%)
Temperature (°C)
2.0
1.5
1.0
0.5
0.0
40
30
20
10
0
150
200
250
300
350
400
450
500

FIG. 7

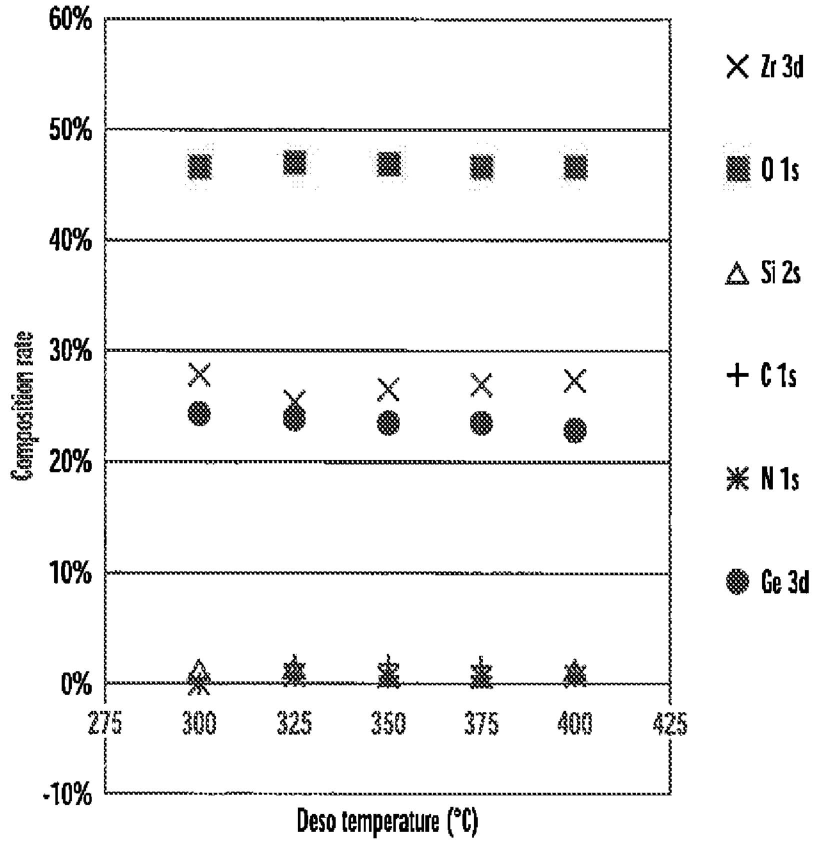

Zr 3d
O 1s
Si 2s
C 1s
N 1s
Ge 3d
Composition rate
Deso temperature (°C)
60%
50%
40%
30%
20%
10%
0%
-10%
275
300
325
350
375
400
425

FIG. 8

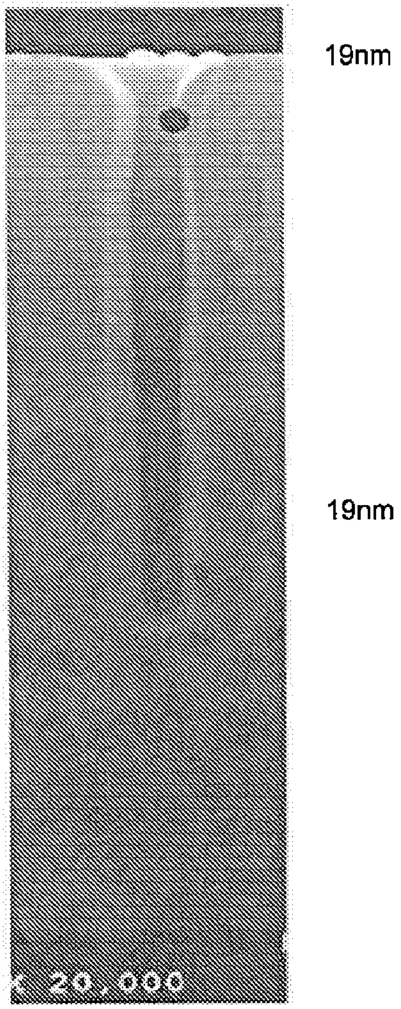


FIG 9

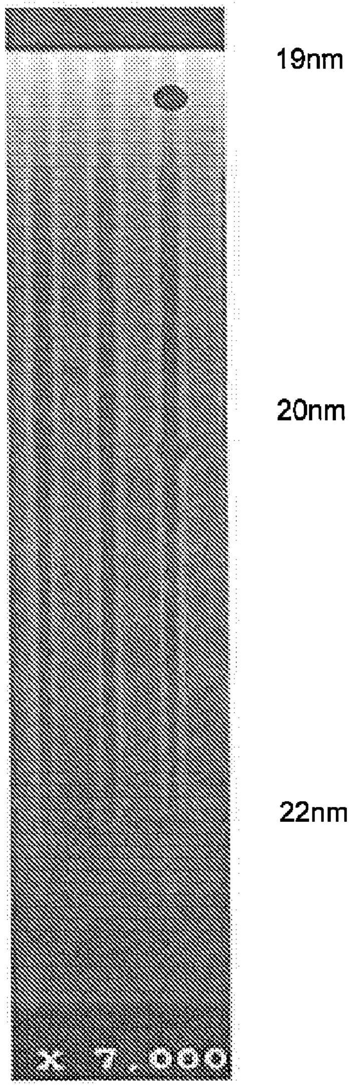


FIG 10

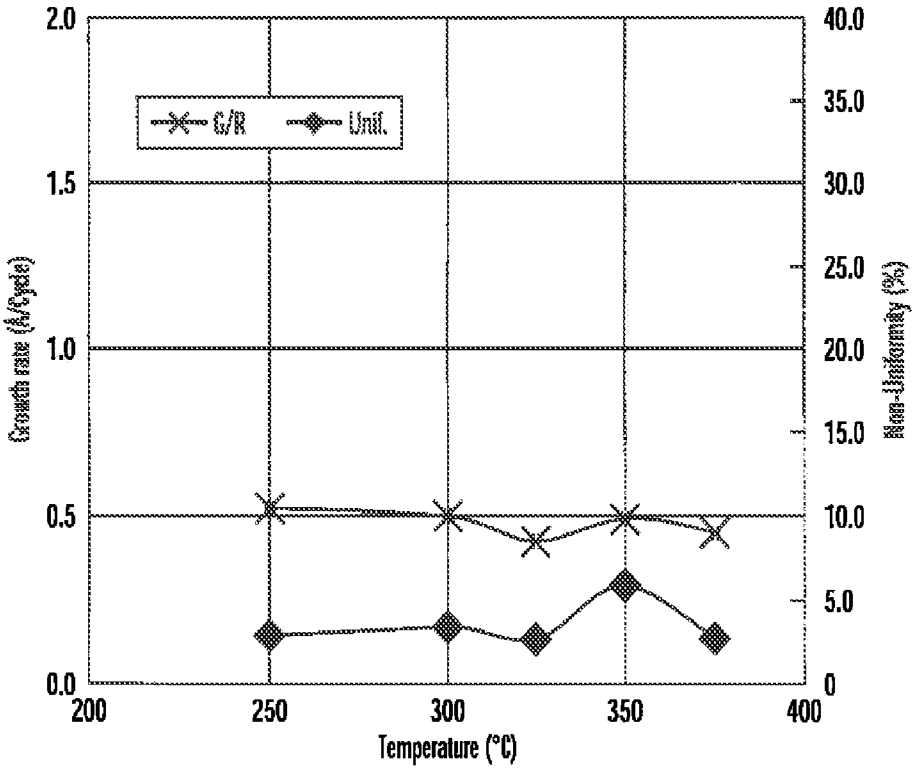

2.0
1.5
1.0
0.5
0.0
Growth rate (Å/Cycle)
G/R
Unif.
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0
Non-Uniformity (%)
200
250
300
350
400
Temperature (°C)

FIG. 11

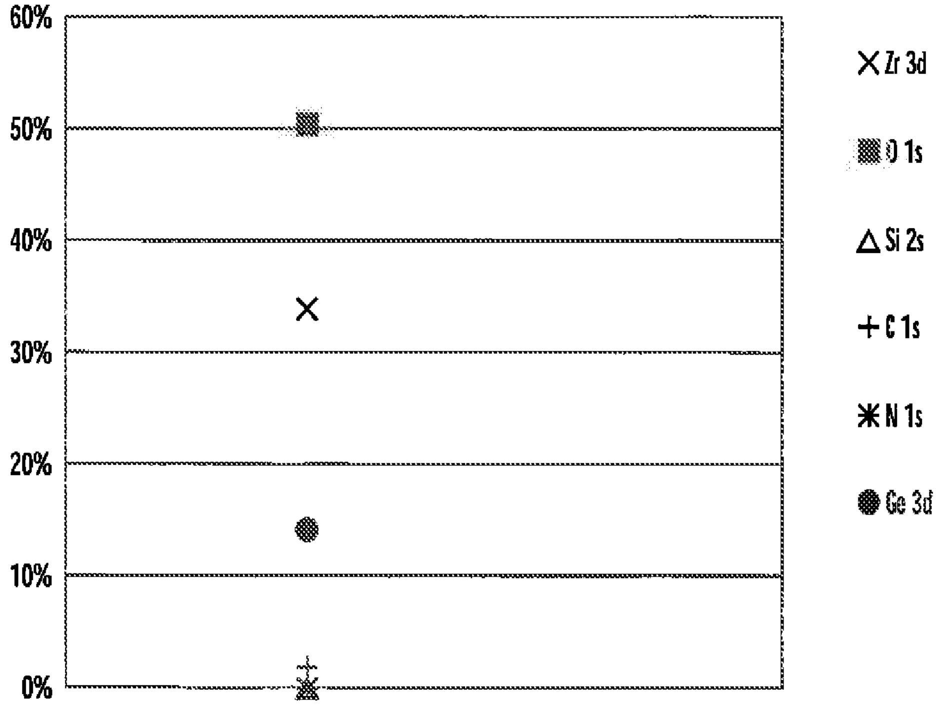

60%
50%
40%
30%
20%
10%
0%
Zr 3d
O 1s
Si 2s
C 1s
N 1s
Ge 3d

FIG. 12

INTERNATIONAL SEARCH REPORT

International application No. PCT/US2015/066434

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. H01L21/316(2006.01)i, C07F7/00(2006.01)i, C07F7/30(2006.01)i, C07F17/00(2006.01)i, C07F19/00(2006.01)i, C23C16/18(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. H01L21/316, C07F7/00, C07F7/30, C07F17/00, C07F19/00, C23C16/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2016
Registered utility model specifications of Japan 1996-2016
Published registered utility model applications of Japan 1994-2016

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	G. CIRUELO et al., Synthesis and reactivity of new silyl substituted monocyclopentadienyl zirconium complexes. X-ray molecular structure of [Zr{η5-C5H4 (SiMe2CH2Ph)}(CH2Ph)3], Journal of Organometallic Chemistry, 1997.12.01, Vol.547, Issue 2, pp.287-296	1-15
A	JP 2005-171291 A (TOSOH CORPORATION) 2005.06.30, whole document (No Family)	1-15

☑ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search: 29.03.2016

Date of mailing of the international search report: 12.04.2016

Name and mailing address of the ISA/JP
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan

Authorized officer
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50 9276
Telephone No. +81-3-3581-1101 Ext. 3559

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/066434

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	X.QIAN et al., Synthesis of new substituted cyclopentadienyl titanium monomethoxydifluorides with BF3·OEt2 as fluorinating reagent and their use in syndiotactic polymerization of styrene, Journal of Organometallic Chemistry, 2004.05.01, Vol.689, Issue 9, pp.1503-1510	1-15
A	WO 2009/036046 A1 (SIGMA-ALDRICH CO.) 2009.03.19, whole document & JP 2010-539710 A & US 2009/0081385 A1 & EP 2191034 A1 & CN 101815807 A & KR 10-2010-0072021 A & TW 200912024 A & CN 103147062 A & KR 10-2015-0139628 A	1-15
A	WO 2007/141059 A2 (L'AIR LIQUIDE SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGERS CLAUDE) 2007.12.13, whole document & JP 2010-506378 A & JP 2009-539237 A & US 2009/0203222 A1 & US 2011/0207337 A1 & US 2009/0311879 A1 & WO 2007/140813 A1 & EP 2029791 A2 & EP 2029790 A1 & EP 2261389 A2 & CN 101896638 A & KR 10-2010-0122962 A & KR 10-2009-0018080 A & CN 101460657 A	1-15
A	WO 2011/020042 A2 (L'AIR LIQUIDE SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGERS CLAUDE) 2011.02.17, whole document & JP 2013-501815 A & US 2012/0207927 A1 & EP 2464652 A2 & EP 2810947 A1 & CN 102712662 A & TW 201114939 A & KR 10-2012-0093165 A	1-15